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Study of poly(acrylic acid) grafted onto polymer surfaces modified by gas phase oxidation techniques

Ameya Khot

STUDY OF POLY(ACRYLIC ACID) GRAFTED ONTO POLYMER SURFACES MODIFIED BY GAS PHASE OXIDATION TECHNIQUES

Ameya Khot

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Materials Science and Engineering

Approved:

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Research Advisor

Dr. Gerald A. Takacs

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Director

Dr. KSV Santhanam

Center for Materials Science and Engineering

Rochester Institute of Technology

Rochester, New York 14623

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Ameya Khot Date

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Table of Contents

List of Figures

List of Tables

ABSTRACT

STUDY OF POLY(ACRYLIC ACID) GRAFTED ONTO POLYMER SURFACES MODIFIED BY GAS PHASE OXIDATION TECHNIQUES

Ameya Khot

Polystyrene (PS) has a wide range of technological applications due to the excellent bulk properties, but does not possess the unique surface properties for applications that require wettability, printability or cell adhesion. The following work focuses on surface modification of polystyrene by different techniques to increase the surface energy and hydrophilicity. UV photo-oxidation of polystyrene was achieved with 253.7 nm and 253.7/184.9 nm radiation in the presence of an atmospheric pressure of oxygen. Contact angle measurements were performed to confirm the surface hydrophilicity with increase in treatment times. Ozone treatment of polystyrene surface was also performed in absence of radiation.

International need for both renewable energy sources and reduction in emission levels has increased interest in a number of electrochemical devices, including batteries and fuel cells, that often use ionic conducting polymer electrolyte membranes such as Nafion® which is a copolymer of tetrafluoroethylene and perfluoro[2-(fluorosulfonylethoxy) vinyl]ether. One disadvantage of Nafion, when applied to a direct methanol fuel cell, is methanol permeation from the anode to the cathode side resulting in poor cell performance. This thesis reports the incorporation of oxygen atoms onto the surface of Nafion-117 using vacuum UV (VUV) photo-oxidation. Acrylic acid, which is hydrophilic, was grafted to the modified PS and Nafion surface. An in-depth chemical state analysis of the surface was studied by X-ray Photoelectron Spectroscopy.

1 INTRODUCTION

Polymers have excellent bulk physical and chemical properties and are easy and inexpensive to process. But most often polymers do not possess the surface properties for applications like adhesion, biomaterials, friction and wear, composites, microelectronic devices etc. Hence, there is a need for surface modification of materials.[1] Recently, many advances have been made to develop surface treatments to tailor the chemical and physical properties at the polymer surface. Virtually all of the surface modification treatments for polymers serve one purpose: to prepare the surface for further treatment. For example, the surface may be modified to increase the strength and quality of the adhesive bonds, prepare the surface for metallization or to increase the affinity of the surface to inks, paints, etc.[2]

1.1 Surface Modification Techniques

Surface modification techniques can generally be classified in the following categories:

1.1.1 Mechanical Abrasion

This is the simplest surface modification technique, e.g., sanding, sandblasting, etc. They have straightforward procedures but it is difficult to control the amount of the material removed from the surface or irregularity of the surface.[2]

1.1.2 Solvent and Chemical Treatments

The solvent attacks the surface causing it to swell, soften and become tacky. Too much solvent may cause the surface to dissolve or distort parts at the interface. Inadequate amount of solvent would make a weak joint. Chemical etching is used to create molecular change on the surface.[2]

1.1.3 Plasma Discharge Process

Polymer surfaces are naturally not receptive to coatings. The plasma discharge provides

both physical and chemical anchoring points for coatings. Unlike the solvent treatments, the plasma discharge process does not produce any waste. Another advantage of this process is the ability to control the extent of change on the surface.[2]

This thesis will investigate the surface modification of Polystyrene and Nafion.

1.2 Polystyrene

Polystyrene (Fig.1) is one of the most widely used thermoplastic because of its excellent physical properties, low cost and ease of fabrication. Due to its extraordinary range of bulk properties, efforts are being made to transform the chemical and physical properties of the polystyrene surface into valuable finished products for wider range of applications. Interaction of cells with biomaterials is one important area of research in biocompatibility and cytotoxicity studies.[3] Polystyrene is generally hydrophobic. This hydrophobic nature inhibits the attachment of a wide range of cell types.[4] Certain applications like cell culture discs[5] require more hydrophilic surfaces, without altering the bulk properties of the polymers. T. G. van Kooten et al.[3] conducted experiments where polystyrene surface was exposed to argon plasma in a reaction chamber followed by ventilation by ambient air. It was observed that endothelial cells were able to adhere and grow and sustain (at least 4 days) only on the surface treated polystyrene surface. Untreated PS surface exhibited negligible cell growth or adhesion. The incorporation of hydroxyl and carboxyl moieties on the polymer surface increases the wettability which improves the cell adhesion.[6, 7] Polystyrene is known to oxidize readily due to the presence of the aromatic structure.[8]

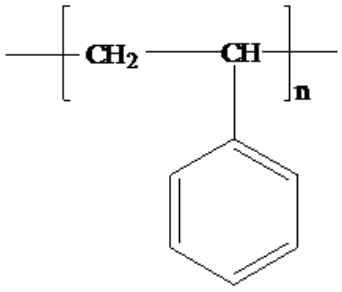

Figure 1: Polystyrene Structure.[9]

D. Zhang et al.[10] exploited this susceptibility of the polystyrene surface to oxidize with ultraviolet or plasma irradiation. The high energy photon interacts with the polystyrene surface causing carbon-carbon chain scission that creates new radicals on the surface. When oxygen gas is introduced into the reaction system, it combines with the free radicals to generate a variety of functional groups like C-O, C=O, or COOH, at the surface. The surface treatment makes the surface hydrophilic and this was confirmed by contact angle measurements.[10]

Superabsorbents are lightly crosslinked functional polymers that can absorb, swell and retain large amount of water. Due to this unique property; superabsorbents have generated interests in specialized areas such as matrices for enzyme immobilization, and controlled release, as well as ordinary personal care products including infant diapers, feminine hygiene products, and incontinence products.[11] Crosslinked poly(acrylic acid) is one such superabsorbent with high water absorbency but the applications are restricted due to the high production costs. Ping-Sheng Liu et al. [11] synthesized novel polystyrene-graft-acrylic acid superabsorbents. The water absorbency of such systems is attributed to the hydrophilic network of acrylic acid that is grafted onto the polystyrene chain. The hydrophilic groups in the network form hydrogen bonds when contacting with water.

Chan-Hee Jung et al.[12] synthesized poly(acrylic acid)-graft-polystyrene beads. The surface change in this study was confirmed using FT-IR and Fluorescence microscope analysis.

1.3 Nafion

During the last few years, serious efforts have been made to stimulate new and efficient ways of energy generation. Environmental concerns and global warming have been the driving forces for these efforts. As these interests have developed, so has the interest in the fuel cell technology. The Direct Methanol Fuel Cell (DMFC) is one of the more approved choices when issues like safety, device fabrication, market, costs, and potential applications are considered. This view is supported by a vast number of research groups, including academic, industrial, and governmental laboratories currently targeting the development of DMFCs for a wide range of potential uses, from portable power sources for small electronic devices to vehicular applications.[13]

However, current DMFCs do not have high energy densities as compared to the Li ion batteries that are the current portable power sources. To create portable DMFCs with high power density, a high concentration of methanol in aqueous solution must be used as the fuel.

During operation (Fig. 2), methanol is fed into the system at the anode; carbon dioxide is generated as follows,

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad \text{(1)}$$

Reduction takes place at the cathode as follows,

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad \text{(2)}$$ [14]

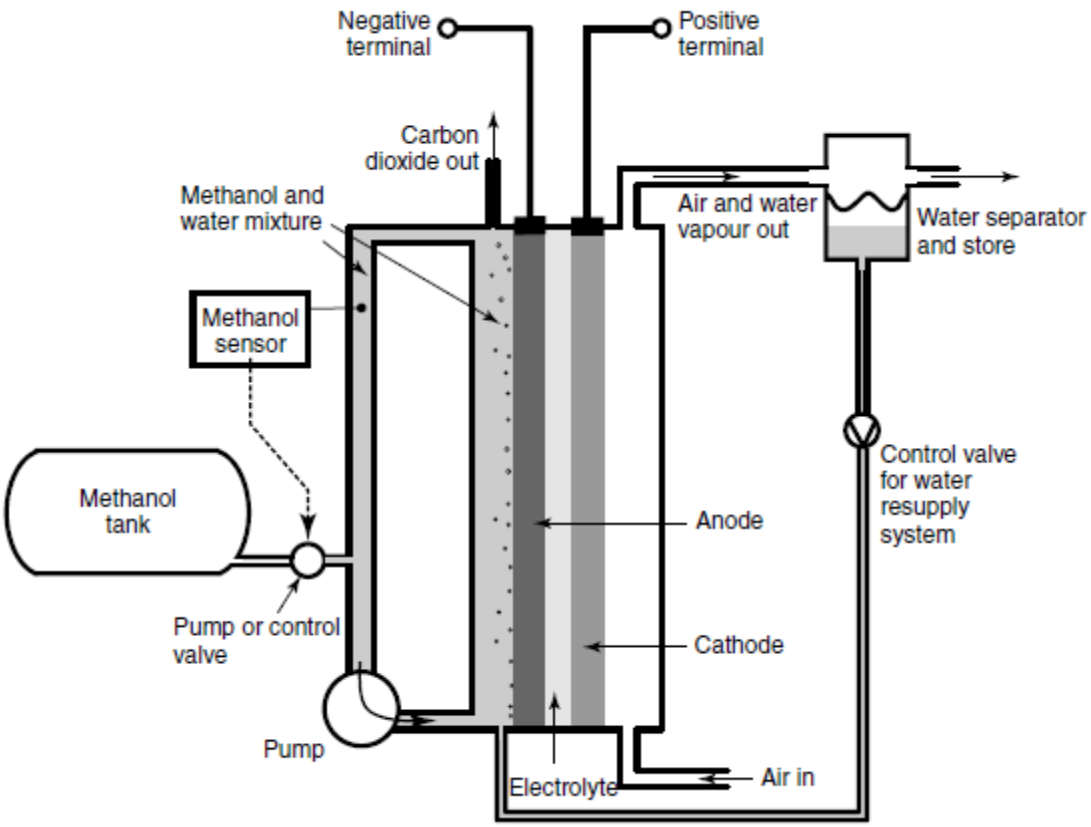

Figure 2: Schematic of a DMFC showing the main components.[15]

The membrane used most widely today is Nafion which was developed over 50 years ago by Dupont. Nafion is a copolymer of tetrafluoroethylene and perfluoro [2-(fluorosulfonylethoxy) - vinyl] ether (Fig. 3). The main features of Nafion include its high chemical resistance and mechanical strength, because of which it can be made into very thin films. HSO_3^- ions are ionically added so that the side chains to the PTFE polymers end with $-SO_3^-$ ions .This creates a combination of $-SO_3^-$ and H^+ ions. The sulphonic acid side chains create the hydrophilic regions in the generally hydrophobic material. Large amount of water can be absorbed due to the hydrophilic regions (Fig. 4). Once the Nafion is hydrated, the H^+ ions are loosely bonded to the SO_3^- ions. This creates a dilute acid. The resultant material with the weak acid regions within the

hydrophobic structure make it possible for the H+ ions to move through the large molecular structure.[15]

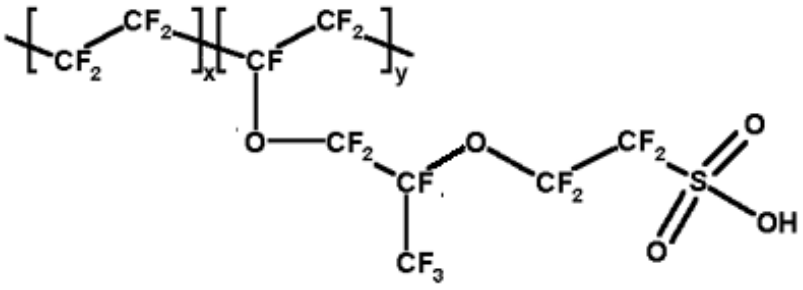

Figure 3: Structure of Nafion polymer [16]

One disadvantage of Nafion, when applied to a direct methanol fuel cell, is methanol permeation from the anode to cathode side resulting in poor cell performance Methanol oxidation can also occur at the cathode, reducing overall performance. Aside from the extent of methanol permeability, a number of other factors have been shown to influence cell output, including the reactivity of the catalyst layers, resistance between electrodes and electrolyte, and the slow diffusion of reactants and/or products. Although all contribute to a lower out-put upon applying a load to the system, only methanol crossover actively decreases the open-circuit voltage (OCV).[13]

Therefore, microwave (MW) and radio-frequency (RF) plasmas have been used to deposit hydrocarbon [17, 18] and fluoropolymer [17, 19] thin films on Nafion to reduce methanol cross-over. Treatment of Nafion with Ar [18,20,21,22] , N_2, H_2 and O_2 [17] MW and RF plasmas, as well as, low dose electron beam exposure[13] results in surface modification which is also effective in decreasing the methanol permeability.

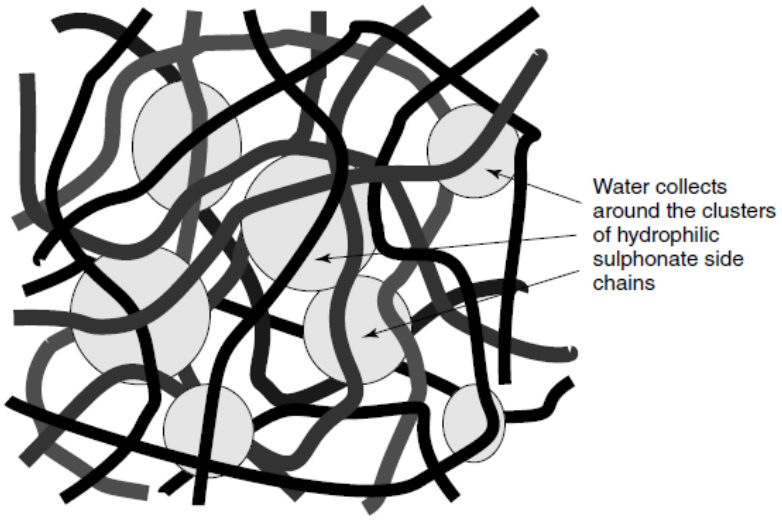

Figure 4: Large Chain Molecules contain the Hydrated Regions along the Sulphonated Side Chains [15]

D. Ramdutt et al.[22] studied the effects of Ar plasma treatment on the Nafion surface. The plasma treatment resulted in defluorination of the Nafion surface. Although the study reported improved hydrophilicity, poor adhesion was detected between the plasma treated surface and the electrodes. Another method to modify the surface would be by graft polymerization. Grafting of vinyl containing monomers, like acrylic acid, onto the chemically activated polymeric matrix is one such example. [23, 24] In grafting, polymer chains are covalently bonded onto the substrate polymer. This approach helps in chemically designing core and shell type system, where core is the polymer matrix and shell is the graft polymer. Mahmoud Nasef et al.[25] used γ-rays to activate the surface of PTFE films in the presence of styrene monomer. This resulted in graft polystyrene copolymers which were subsequently sulfonated to provide large sulfonic acid groups on the surface.

2 RESEARCH AIM

In this thesis, the following investigations were performed,

1. UV photo-oxidation of polystyrene surface at room temperature and atmospheric pressure using low pressure mercury lamps that emit 184.9 nm and 253.7 nm wavelengths and low pressure mercury lamps that emit only 253.7 nm wavelength.
2. Ozone treatment of polystyrene surface in absence of radiation.
3. Grafting copolymerization of the poly(acrylic acid) onto polystyrene that was activated using the above techniques.
4. VUV photo-oxidation of Nafion using downstream Ar plasma, followed by grafting of poly(acrylic acid) onto the activated Nafion surface.

3 EXPERIMENTAL

3.1 Materials

3.1.1 Polystyrene

Commercially available 0.125 mm thick biaxially oriented polystyrene films $(C_8H_8)_n$ were purchased from Goodfellow Corp, Huntington, England. The polystyrene films were cleaned by ethanol in an ultrasonic bath for 15 min to remove any possible dust, grease or oil contamination. The films were stored in a dessicator that contained anhydrous calcium sulfate, for a minimum of 24 hours. The films were later stored in a Petri- dish on a filter paper until the photo-oxidation. X-ray Photoelectron Spectroscopy confirmed the surface of the cleaned polystyrene film. The polystyrene film of dimensions 2.3 cm X 2 cm was cut, so that it stands vertically in the cylindrical photochemical cell.

3.1.2 Nafion

Nafion®-117, perfluorinated membrane, with 1100 g equivalent weight and 0.007 inch in thickness was obtained from ALDRICH® St. Louis, MO. The Nafion samples were cut to 1 square cm size and cleaned by the following 3 steps process: (1) boiling for 1 hour in 1M solution of sulfuric acid. This step exchanges the cations in the membrane with protons. (2) Boiling in 3% hydrogen peroxide solution for one hour. This cleaning gets rid of the organic contamination in the membrane. (3) Boiling in deionized water for one hour and drying in dessicator to a constant mass.[20]

3.1.3 Acrylic acid

Acrylic acid **(**Fig. 5**)** containing 0.02% hydroquinone monomethyl ether inhibitor was purchased from Fluka. The inhibitor was removed by vacuum distillation process as shown in Fig. 6.

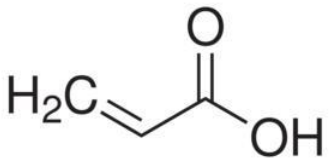

Figure 5: Acrylic Acid Structure [26]

Figure 6: Set-up for Vacuum Distillation.

Iron sulfate heptahydrate (99% purity) was purchased from Sigma-Aldrich and L-ascorbic acid (99.5 % purity) was purchased from J. T. Baker.

3.2 UV Photo-oxidation

A Rayonet photochemical chamber (manufactured by Southern New England Ultraviolet Co., Inc., Branford, CT) was used for the UV photo-oxidation as well as ozone treatment of the samples. The chamber contains 16 mercury lamps. Two types of lamps (Fig.7) were used in this study, for 253.7nm irradiation and for 184.9/253.7 nm irradiation.

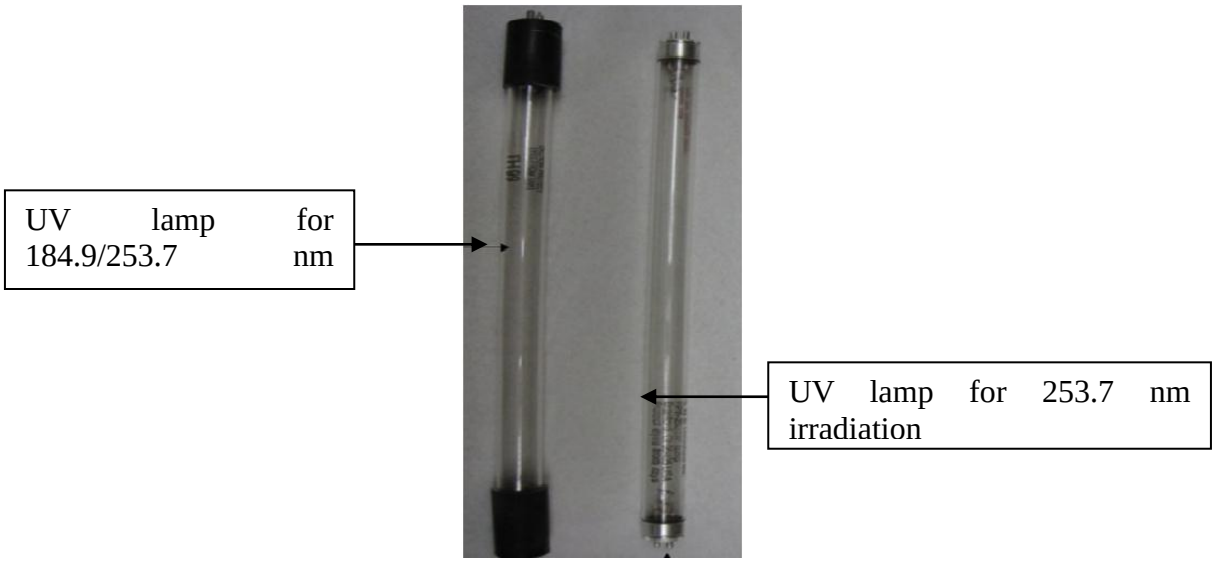

Figure 7: Mercury lamps used for UV irradiation

The sample film was placed in a cell constructed of Suprasil® (Fig. 8). Prior to the UV irradiation, high purity oxygen (99.99 %) was flowed through the cell for 10 min to displace the air present in the cell. Simultaneously, nitrogen was flown through the Rayonet chamber to displace the air.

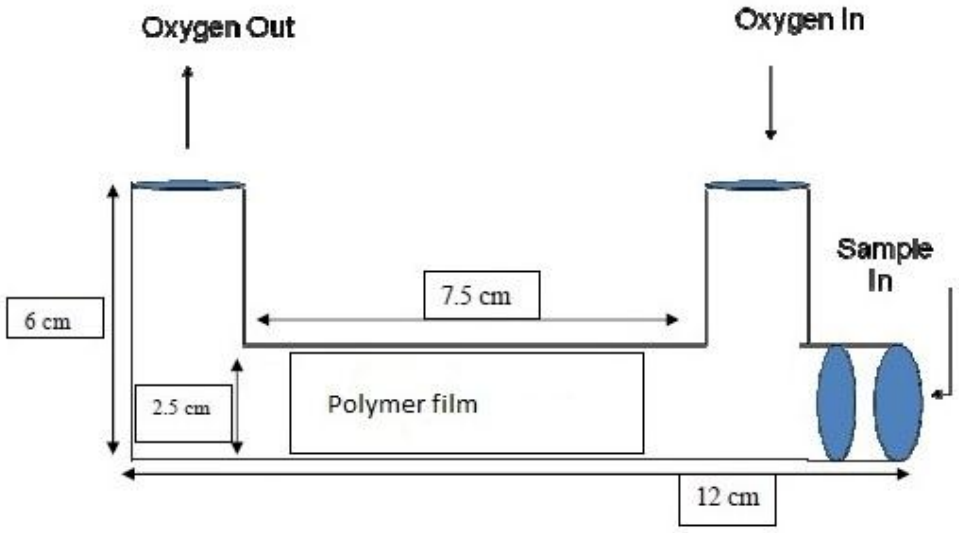

Figure 8: Quartz Suprasil cell for UV photo-oxidation

The polymer film was placed vertically inside the cell so that it is parallel to the UV lamps to allow treatment on both sides of the film. The polymer surface was then photo-oxidized using the UV/oxygen mixture for different treatment times at constant flow rate of oxygen (43 cm^3/min).

Nitrogen molecule is transparent to the UV radiation while the ground state oxygen molecule absorbs the 184.9 nm photons (Fig. 9) to break into two ground state O (^3P) atoms as shown in reaction (3).[27]

$O_2 + h\nu = O(^3P) + O(^3P)$ $\lambda \leq 242.4$ nm..... (3)

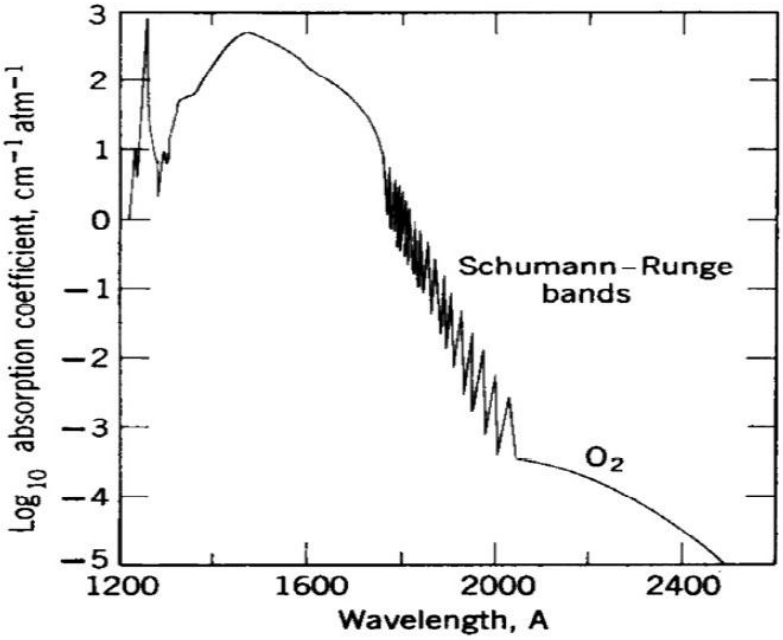

Figure 9: Photo-absorption spectrum for oxygen [18]

Ozone which is formed in the photochemical cell by reaction (4) involving a stabilizing molecule M,

$O(^3P) + O_2 + M = O_3 + M$..... (4)

3.3 Ozone Treatment in the Absence of Radiation

For ozone treatment of the polystyrene samples in the absence of radiation, the film was kept in the cell that was placed outside the photochemical reaction chamber. The ozone was formed in the empty cell inside the photochemical chamber, which was flown to the film placed outside the chamber (Fig.10). This setup allowed the study of the reaction of ozone with the polystyrene surface without any photons incident directly on the surface.

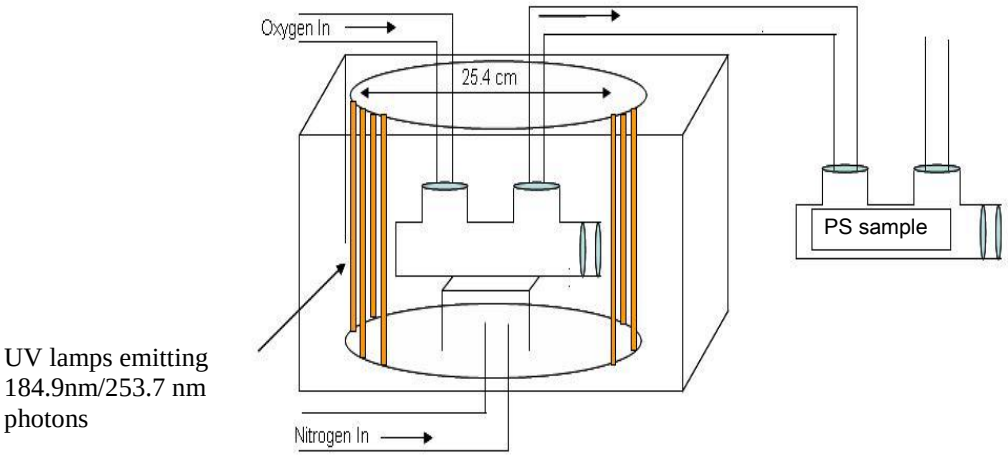

Figure 10: Experimental Set-up for Ozone Treatment of Polystyrene.

3.4 VUV Photo-oxidation

Low-pressure argon MW plasmas, operating at a frequency of 2.45 GHz and absorbed power in the range of 25-44 W (the difference between the forward and reflected power) were used as the source of VUV radiation and oxygen atoms to modify the surface of the samples located downstream from the plasmas. For VUV photo-oxidation, the Nafion sample was placed 23.8 cm downstream from the vertical MW discharge of Ar. Oxygen was introduced into the vacuum system about 3 cm above the sample (Figs. 11 and 12). The argon and oxygen flow rates

were 50 and 10 cm^3/min, respectively. The reaction chamber pressure was maintained at 0.515 - 0.535 torr. At the reaction time associated with this distance, charged particles and metastables from the plasma contribute negligibly because of recombination and deactivation processes occurring in transit to the sample.

Nafion samples were pasted on microscope slides by double-sided tape and then the slides were put on a cylindrical stainless steel holder which stands in the center of reactor's chamber.

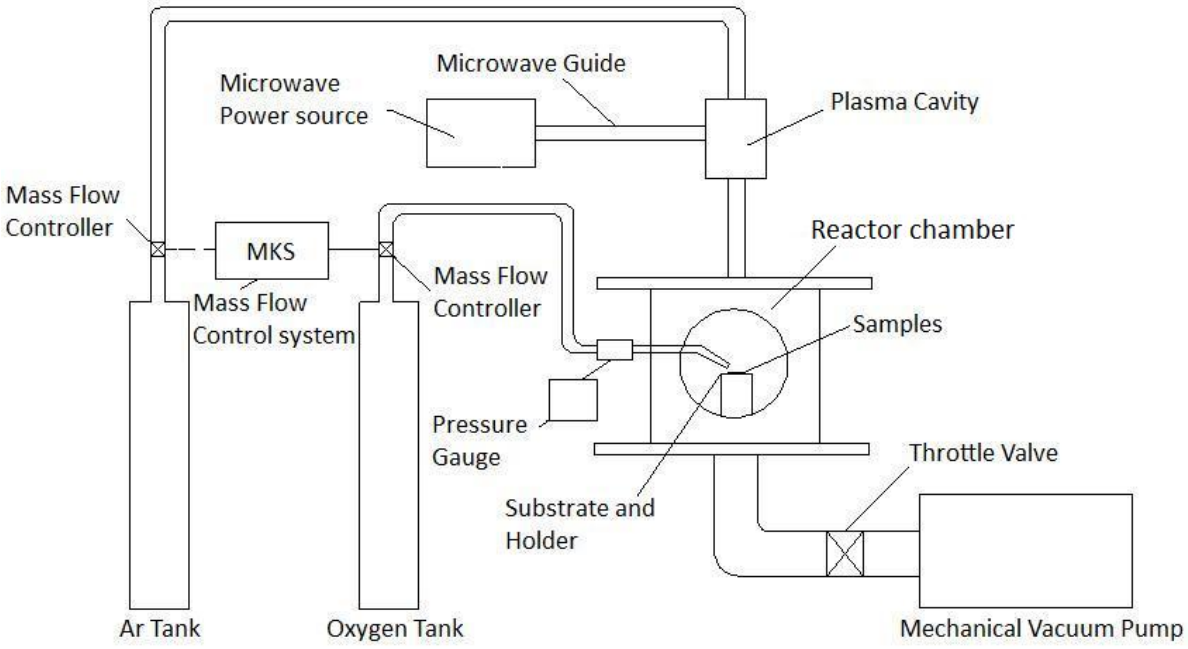

Figure 11 Schematic of a VUV photo-oxidation from downstream Ar plasma.

Figure 12: The vertical plasma cavity for VUV Photo-oxidation of Nafion

3.5 X-ray Photoelectron Spectroscopy (XPS)

XPS is a versatile analysis technique to analyze polymer surface. In XPS the sample surface is irradiated with X-rays. The X-ray photons interact with the inner shell electron, which results in complete transfer of photon energy to the electron. This knocks the electron out of the sample surface (Fig. 13). An electron analyzer measures the kinetic energy of the released photo-electron.

The difference between the incident photon energy (hv) and kinetic energy (KE) of the photoelectron is the binding energy (BE) of the inner shell electron as shown in equation (5). The binding energy for the particular shell of the atom is unique for each element [4].

$$BE = h\nu - KE \quad \ldots\ldots (5)$$

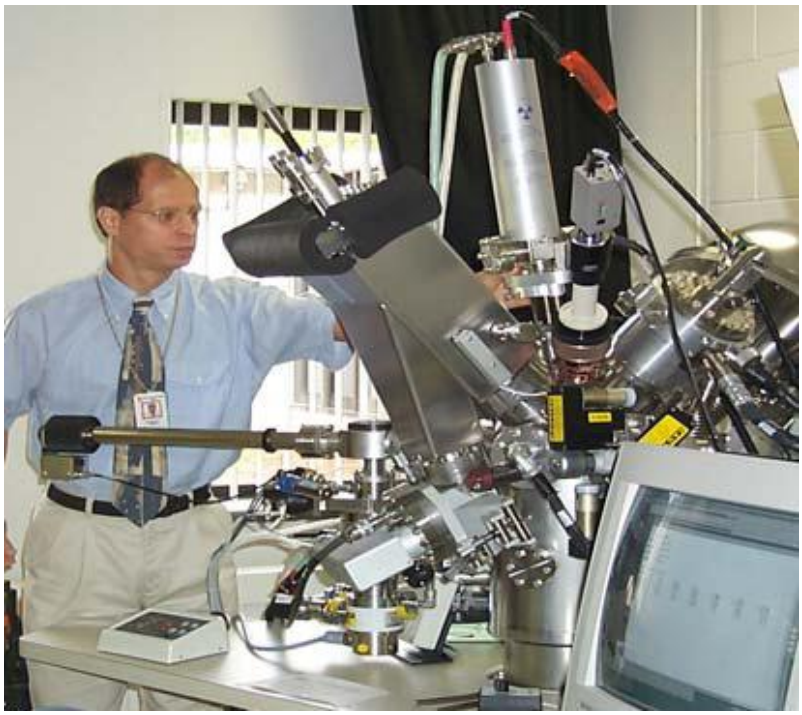

Figure 13: XPS Physical Electronics Model 5800 at Xerox Corp. Webster, NY.

The top 2 -5 nm of the sample surfaces were analyzed by a Physical Electronics Model 5800 XPS using a take-off angle of 45º between the sample and analyzer. A region of about 800 μm in diameter was analyzed. The sample films were prepared by cutting sections from the sample provided and mounting them beneath a molybdenum sample mask for presentation to the beam. The monochromatic Al K_α (1486 eV) x-ray beam irradiated the sample and the electron optics of the analyzer was focused to accept the photoelectrons emitted from the polymer sample. The quantitative analyses are precise to within 5% relative for major constituents and 10% relative for minor constituents. The samples were charge-neutralized with a flood of low energy electrons from a BaO field emission charge neutralizer. This method of analysis minimized radiation damage to the samples.

The method used for curve fitting of the observed chemical states is as follows:

1. Use the control polystyrene C 1s spectrum as the model for the spectrum of an untreated

material.

2. Subtract the control C 1s spectrum from the spectrum for the treated sample.
3. Curve fit the remainder spectrum to determine the number of peaks their binding energy and peak widths resulting from treatment.
4. Use the peaks from curve fitting the remainder spectrum to curve fit the total treated spectrum. Missing peaks are then added to the curve fitting of the treated sample to achieve a good chi square fit – peaks due to energy loss must be weak.
5. Perform a materials balance test to see if the results of the curve fitting agree with the oxygen concentrations as determined from the quantitative analyses.

3.6 Goniometry

Contact angle Goniometer was used to measure the wettability of the treated surface. The static contact angle that a drop of water makes with the polystyrene surface was measured for different treatment times. Polystyrene is generally hydrophobic, and surface photo-oxidation makes the surface more hydrophilic (Fig. 14). Contact angle measurement has often been used to determine the hydrophilicity of polystyrene. The contact angle is found to decrease with the increase in surface oxygen content. [28] [29]

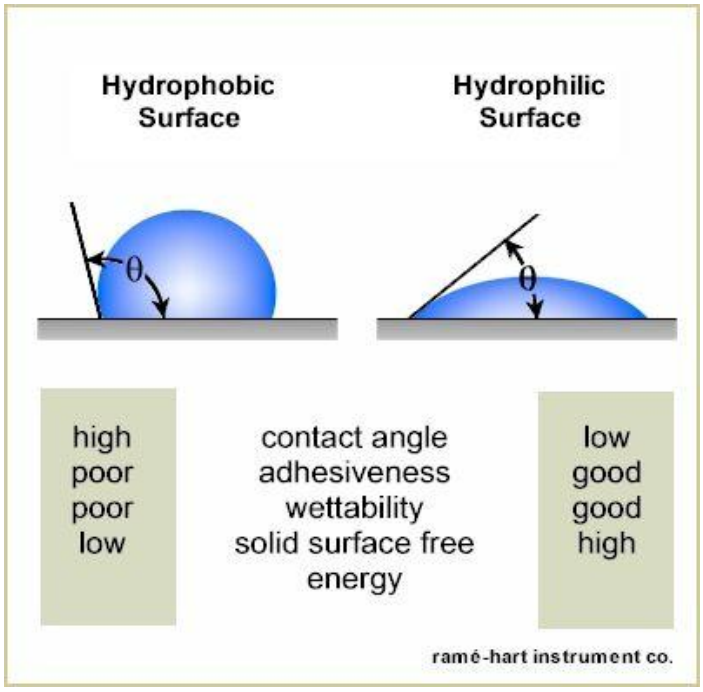

Figure 14: The Polymer Surface becomes more Hydrophilic with Surface Treatment over time. The Contact Angle reduces with Increase in Surface Oxygen Content [30]

The polystyrene film was mounted on the support. A 10 microliter syringe was used to manually dispense a drop of water on the treated surface. The contact angle is measured through the calibrated eyepiece. The intensity of the light source can be adjusted to provide a clear image.

Figure 15 Contact Angle Goniometer used to Study the Hydrophilicity of the Surface over Treatment Times. [30]

3.7 Grafting Experiment

Prior to grafting, the Nafion and polystyrene samples were activated with VUV and UV photo-oxidation, respectively. The treated surfaces were analyzed by XPS. Following photo-oxidation, the surfaces were graft polymerized with a water solution of acrylic acid (6.8 M) in a round-bottom flask (Fig.16). After the solution was purged with dry argon for 15 min, iron sulfate heptahydrate and L-ascorbic acid were added with concentrations 0.010 and 0.014 M, respectively. The Fe^{2+} ions act as a reducing agent for non-graft polymerized materials while ascorbic acid acts as a co-reducing agent to regenerate Fe^{2+} from Fe^{3+} [16] The surface-activated polymer samples were added and the reaction conducted at 65 ^{o}C while purging with argon for 1.5 hours. After the reaction was complete, the samples were collected, washed with hot de-ionized water, heated in de-ionized water at 65 - 80 ^{o}C for 2 hours in order to remove unreacted acrylic acid and then dried in a dessicator to constant mass.

Figure 16: Experimental set-up for Grafting polymerization

4 RESULTS

4.1 Surface Modification of Polystyrene by 184.9/253.7 nm radiation

4.1.1 Surface Activation of Polystyrene by UV Photo-oxidation (184.9/253.7nm radiation)

4.1.1.1 Qualitative Analysis

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon and oxygen on the surface of every sample. The samples treated for 5, 15 and 60 minutes also contained nitrogen.

4.1.1.2 Quantitative Results

Quantitative analyses were obtained for the samples. The results of the analyses are summarized in Table 1.

Sample	At% C	At% O	At% N
PS0 control	98.8	1.2	0.0
4PS2 2 min	88.8	11.2	0.0
4PS5 5 min	70.2	28.9	0.9
4PS15 15 min	64.5	34.0	1.5
4PS60 60 min	59.6	38.4	2.1

Table 1: Results of the Quantitative XPS Analyses for the Polystyrene Films (Photo-oxidized by 184.9/253.7nm irradiation)

The concentration of oxygen as a function of treatment time is shown in the plot below. The oxygen concentration increased rapidly for the first 15 minutes and then increased slowly over the next 45 minutes (Fig 17).

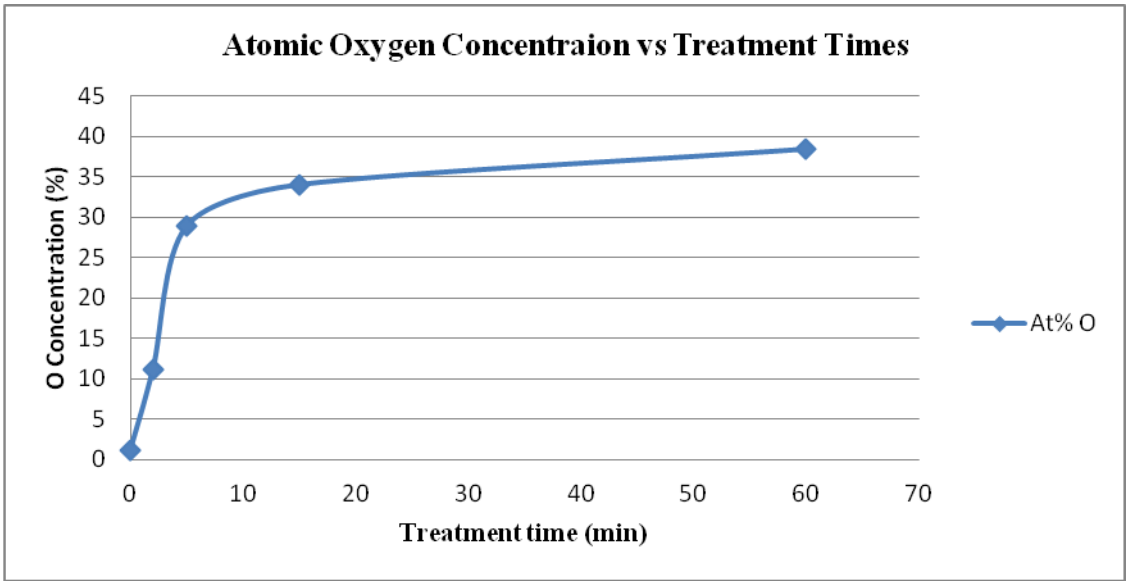

Figure 17: Atomic Oxygen Concentration vs. Treatment Times for PS Films (Photo-oxidized by 184.9/253.7 nm irradiation)

4.1.1.3 Chemical State Analysis

Figure 18 illustrates the C 1s spectrum for the polystyrene control. The energy loss structure associated with the Π→Π* transition is evident at about 291.7 eV. Figure 19 shows the C 1s overlapped spectra obtained from the control and treated samples. The principal peak at 285 eV is due to carbon-carbon bonding. The manifold of peaks with binding energies greater than 285 eV are due to carbon-oxygen bonding. The peak due to Π→Π* energy loss satellite at about 292 eV becomes weaker after treatment of the polystyrene. This is indicative of the breaking of the phenyl ring. In order to determine the chemical species present on the surface the C 1s and O1s peaks were curve fit.

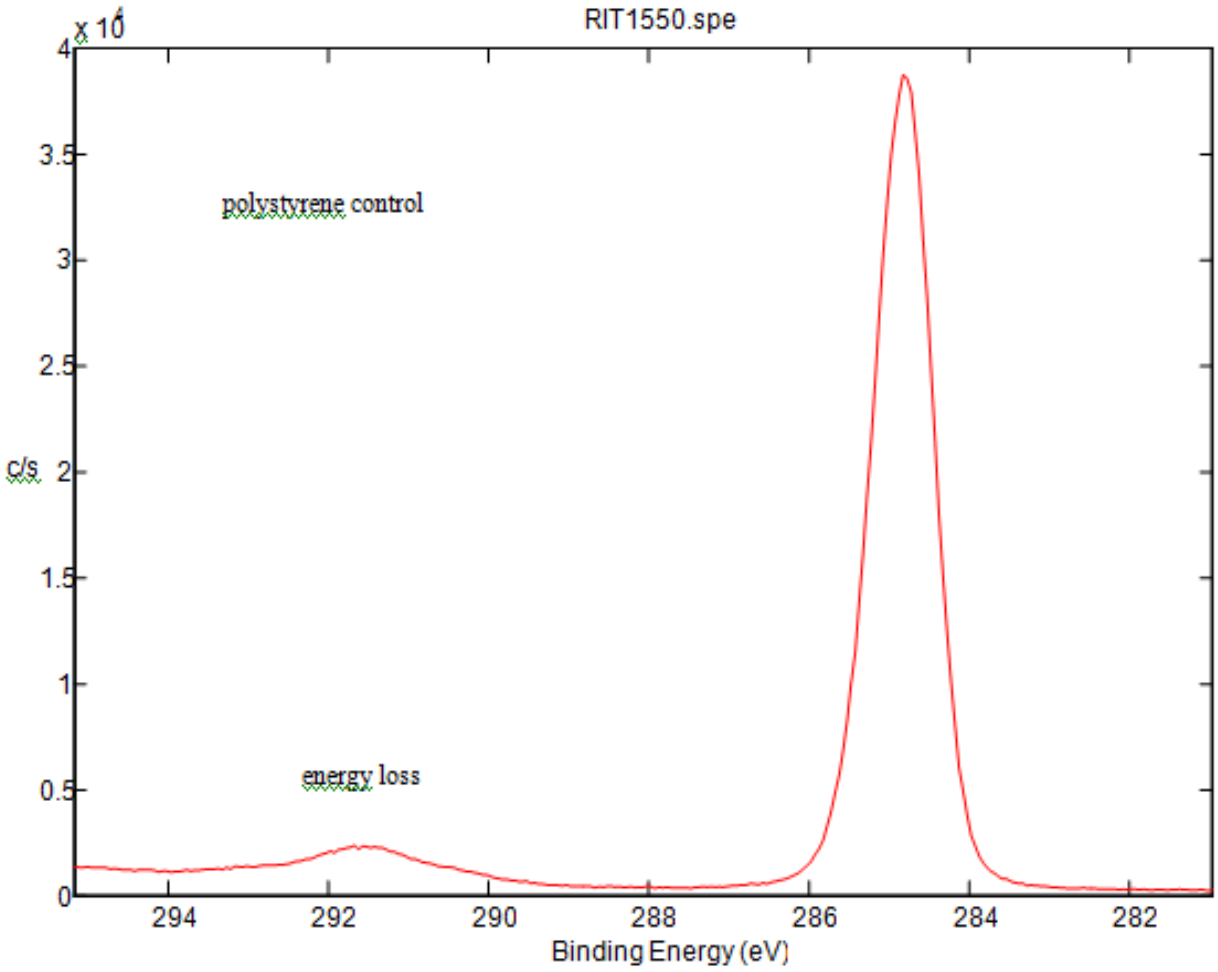

Figure 18: C 1s spectrum for the polystyrene control

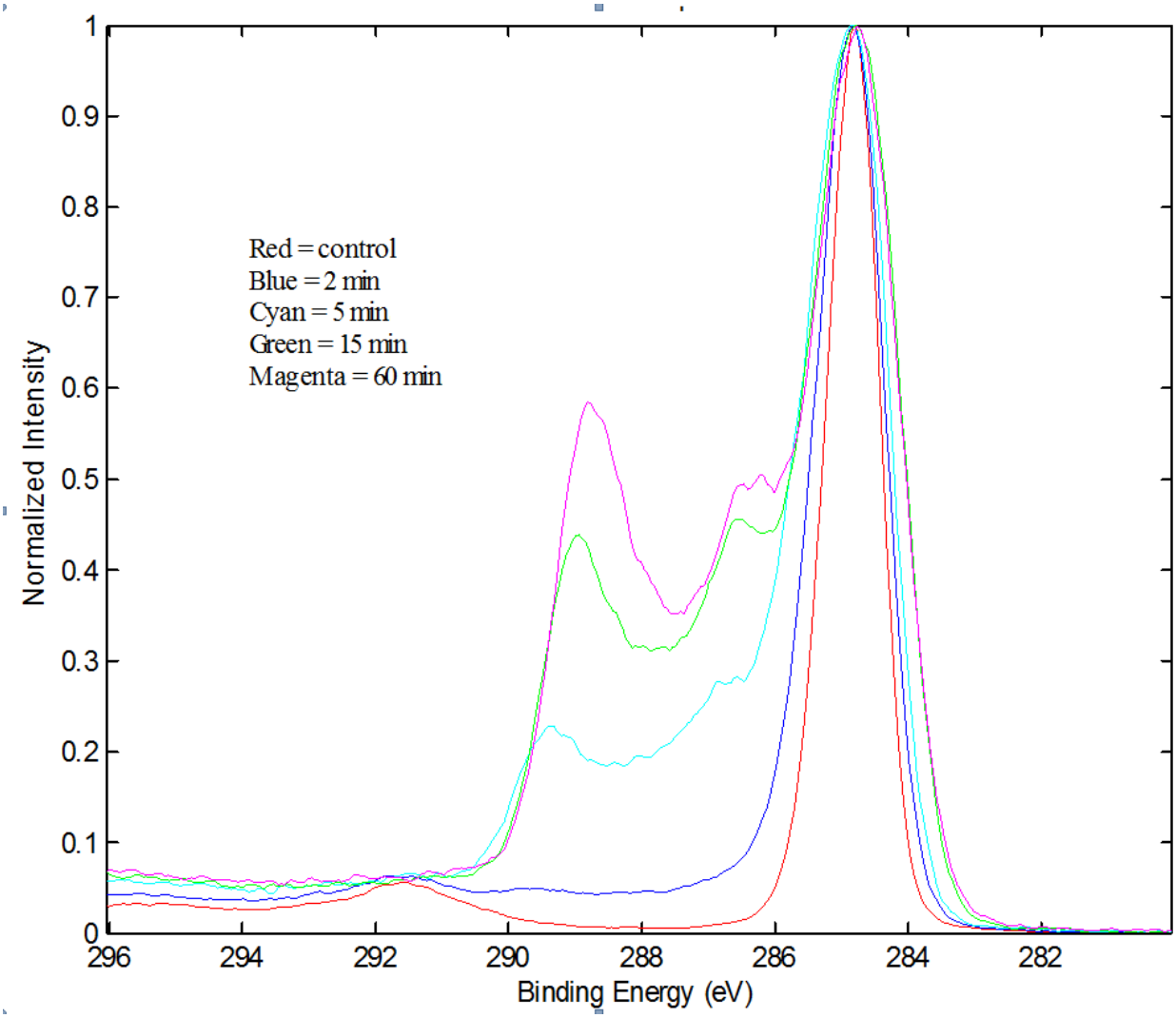

Figure 19: Overlapped C 1s Spectra for Control and Treated PS films Films (Photo-oxidized by 184.9/253.7 nm irradiation)

The results of the curve fitting for the C 1s peaks are summarized in Table 2. The possible species that are the origins of the peaks are identified in Table 3. The major contributors to the C 1s spectra are the aromatic carbons. The amount of carbon-oxygen bonding increased very rapidly for the first few minutes and then approached a plateau after about 15 minutes of treatment followed by a slow gradual increase. As the length of treatment increased the amount of carbon singly bonded to oxygen decreased slightly and the amount of C=O and acid/lactone

groups increased. There was a corresponding decrease in the carbon-carbon bonding. The amount of carbon-carbon bonding due to the aromatic ring decreased as evidenced by the significant decrease in the energy loss structure associated with the Π→Π* transition (292 eV).

Binding Energy (eV)	Control	2 min	5 min	15 min	60 min
284.6	96.0	82.6	51.9	44.9	40.2
285.5	0.0	9.7	15.5	9.2	9.0
286.4	0.2	0.0	13.1	18.7	19.7
287.7	0.2	2.0	8.3	11.1	13.1
289.3	0.0	2.0	9.0	15.5	17.1
291.5	3.7	3.7	2.1	0.5	1.0

Table 2: Peak Areas for C 1s Peaks as Determined by Curve Fitting the C 1s Spectra Films (PS films Photo-oxidized by 184.9/253.7 nm irradiation)

Binding Energy (eV)	Species within Binding Energy Range
284.6	C-C aromatic ring
285.0	C-C alkyl
285.4	ketone, ester, lactone, anhydride
286.4	alcohol, ester
288.0	Ketone
288.5	ester
289.3	acid, lactone, anhydride
291.5	Energy loss peak

Table 3 Assignment of C 1s Peaks by Binding Energ[31]

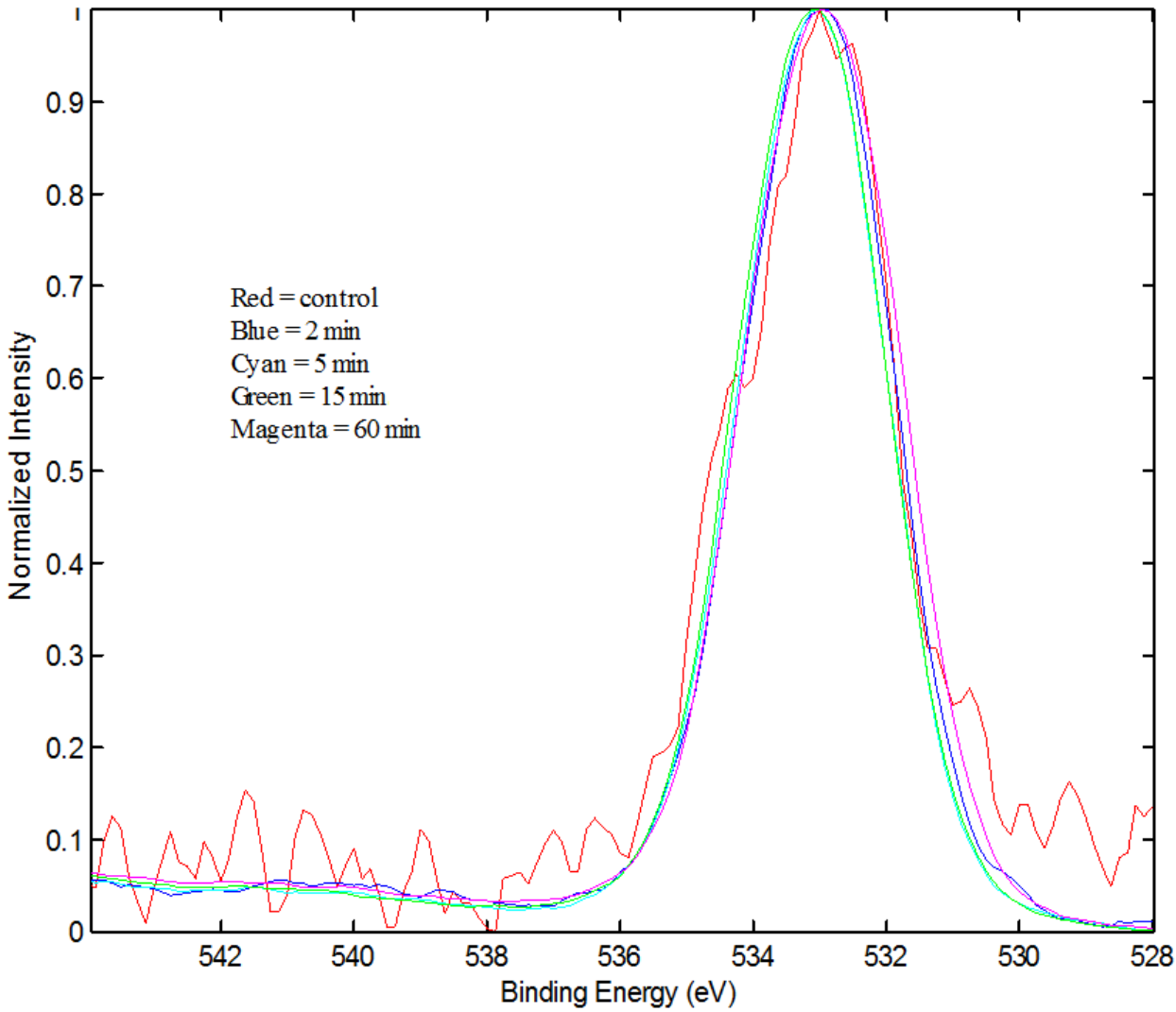

Figure 20 : Overlapped O 1s spectra for the PS films (Photo-oxidized by 184.9/253.7 nm irradiation).

Figure 20 shows the overlapped O 1s spectra for the samples. The spectra formed broad Gaussian peaks that made it difficult to extract information concerning the carbon-oxygen bonding. Curve fittings were performed and the results are summarized in Table 4. Literature values[31] for the various species are summarized in Table 5. Due to the lack of energy resolution the O 1s spectra did not provide much additional information not already gained from the C 1s spectra. At short treatment times the O 1s spectra indicate the formation of hydroxyls and

carbonyls (ketones). Longer treatment times resulted in an increase in the amount of esters, acid and lactone generated.

Binding Energy (eV)	control	2 min	5 min	15 min	60 min
532.0	3.4	31.3	44.0	57.3	51.6
533.0	57.0	43.8	38.0	37.3	45.0
533.7	39.6	24.5	18.0	5.4	3.4

Table 4: O 1s Peak Areas as Determined by Curve Fitting Films (PS films Photo-oxidized by 184.9/253.7 nm irradiation)

Binding Energy (eV)	Potential Species
532.2 – 532.4 eV	Ester, acid, lactone, ketone
532.5 – 532.7 eV	Ether, alcohol, anhydride
533.5 eV	Ester, acid, lactone
533.9 eV	Anhydride

Table 5: Assignment of O 1s Peaks by Binding Energy[31]

4.1.1.4 Contact Angle Measurements

The Contact Angle measurements are summarized in Table 6. The contact angle rapidly decreased during the first 15 min of treatment times and decreased slowly for the next 45 minutes (Fig. 21).

Sample	Contact Angle
PS0 control	84˚
4PS2 2 min	63˚
4PS5 5 min	38˚
4PS15 15 min	23˚
4PS60 60 min	17˚

Table 6: Contact Angle Measurements on the Treated PS Surfaces (Photo-oxidized by 184.9/253.7 nm irradiation).

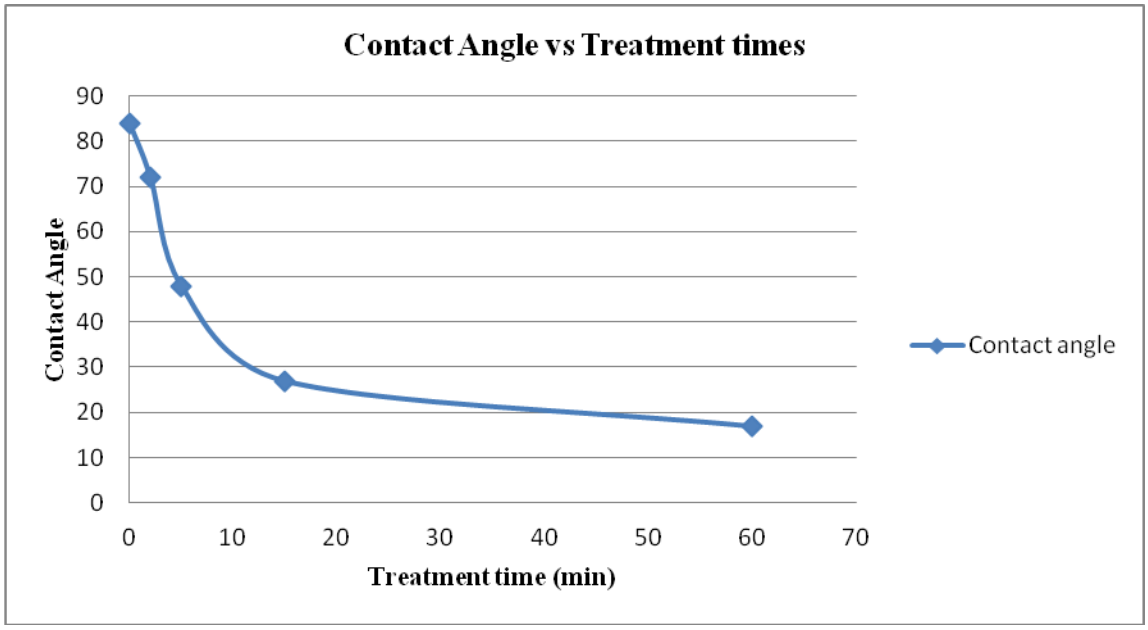

Figure 21: Contact Angles vs. Treatment times for PS films (Photo-oxidized by 184.9/253.7 nm irradiation)

4.1.2 Grafting onto 184.9/253.7 nm surface treated Polystyrene

4.1.2.1 Qualitative Analysis

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon and oxygen on the surface of all five samples. Sample G-4PS2 contained fluorine possibly due to

fluoropolymer contamination.

4.1.2.2 Quantitative Results

Quantitative analyses were obtained for the samples. The results of the analyses are summarized in Table 7.

Sample	At% C	At% O
G-4PS0 control	84.96	15.04
G-4PS2 2 min	Contaminated	Fluoropolymer
G-4PS5 5 min	84.53	15.47
G-4PS15 15 min	83.43	16.57
G-4PS60 60 min	80.43	19.57

Table 7: Results of the Quantitative XPS Analyses for the PAC Grafted Polystyrene Films

4.1.2.3 Chemical State Analysis

Figure 22 illustrates the C 1s spectrum for the PAC grafted to a polystyrene control. Figure 23 shows the overlapped C 1s spectra obtained from a control and samples treated for 5, 15 and 60 minutes. The principal peak at about 285 eV is due to alkyl and aromatic carbon-carbon bonding. Peaks with binding energies greater than 285 eV are due to carbon-oxygen bonding. The loss of phenyl groups from the surface is evident since the peak due to $\Pi \rightarrow \Pi^*$ energy loss satellite becomes weaker after treatment of the polystyrene.

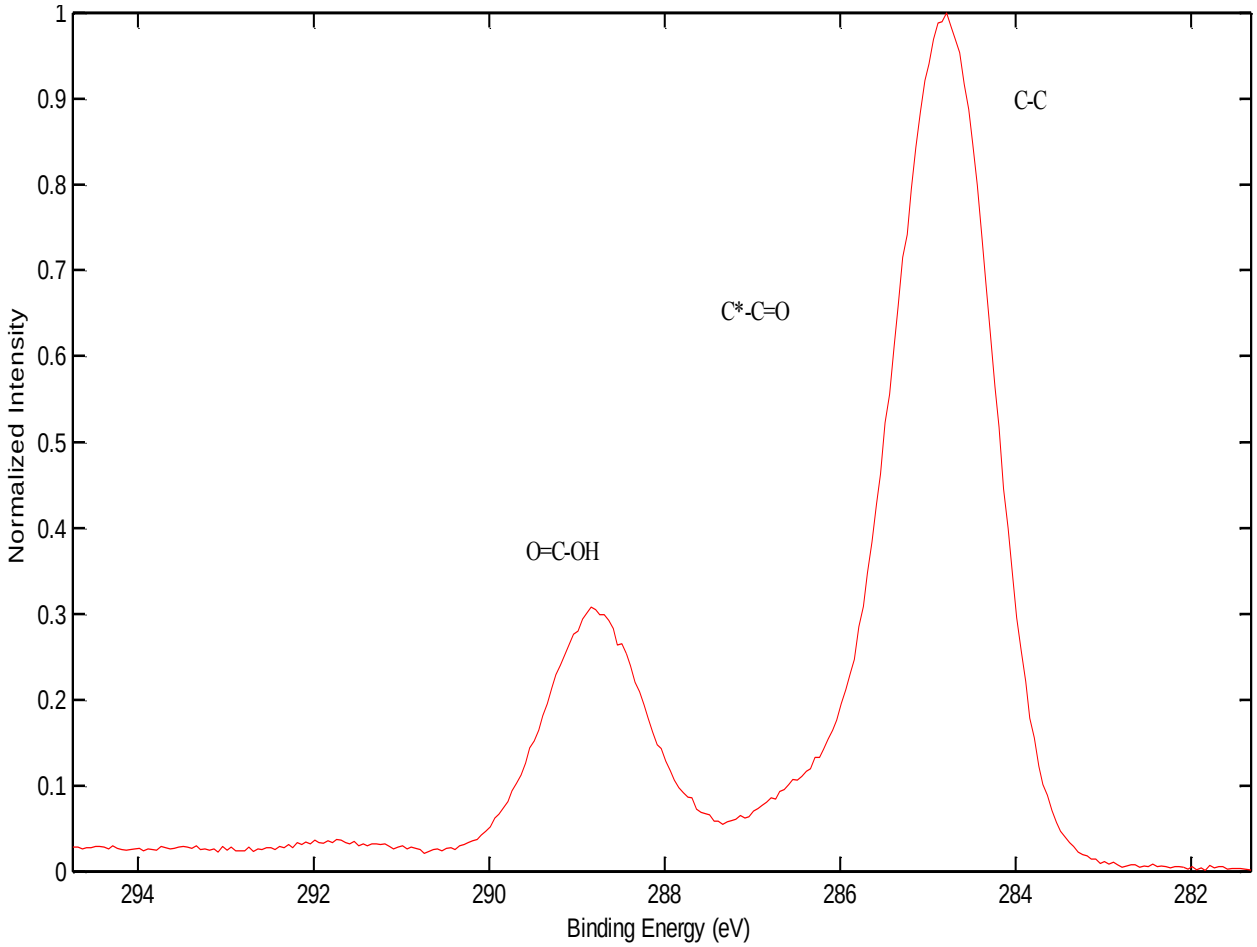

Figure 22: The C 1s spectrum for the PAC grafted to the control polystyrene sample

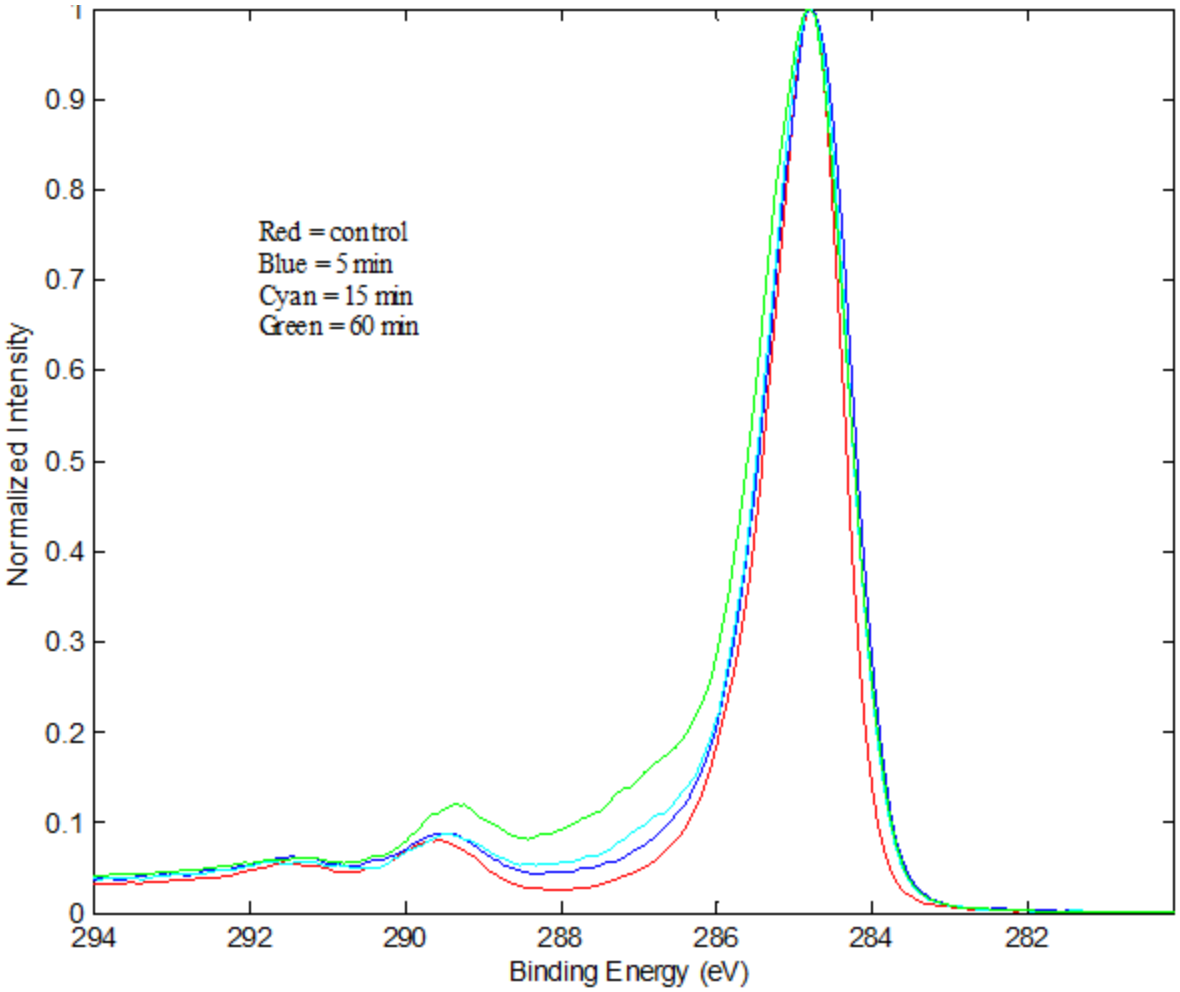

Figure 23: Overlapped C 1s Spectra for PAC Grafted Treated Polystyrene (Photo-oxidized using 184.9/253.7 nm irradiation)

The results of the curve fitting for the C 1s peaks are summarized in Table 8. Possible species that are the origins of the peaks are identified in Table 3. The major contributors to the C 1s spectra were the aromatic carbons. There is a gradual increase in the concentration of carbonyl groups (289.3 eV). The samples exhibit weak peaks due to acid. This suggested that some PAC is present on the surface. The amount of carbon-carbon bonding due to the aromatic ring decreased as evidenced by the significant decrease in the energy loss structure associated with the $\Pi \rightarrow \Pi^*$ transition.

Binding Energy (eV)	0 min	5 min	15 min	60 min
284.6	62.7	67.7	69.4	60.3
285.2	25.5	18.7	16.6	18.4
286.4	4.8	4.6	5.7	8.5
287.7	0.0	1.2	1.9	4.8
289.3	4.2	4.5	4.0	5.7
291.5	2.9	3.3	2.4	2.5

Table 8: Peak Areas for C 1s Peaks as Determined by Curve Fitting the C 1s Spectra for PAC Grafted Treated Polystyrene (Photo-oxidized using 184.9/253.7 nm irradiation)

The broad Gaussian peaks in the overlapped O 1s spectra (Figure 24) made it difficult to extract information concerning the carbon-oxygen bonding. Curve fittings were performed and the results are summarized in Table 9. Literature values[31] for the various species are summarized in Table 5. Due to the lack of energy resolution the O 1s spectra do not provide much additional information not already gained from the C 1s spectra. The low binding energy peak is more intense then the high binding energy peak. This is due to exposed oxidized polystyrene that is not grafted with PAC. The treated polystyrene samples contained more oxygen than the grafted polystyrene samples.

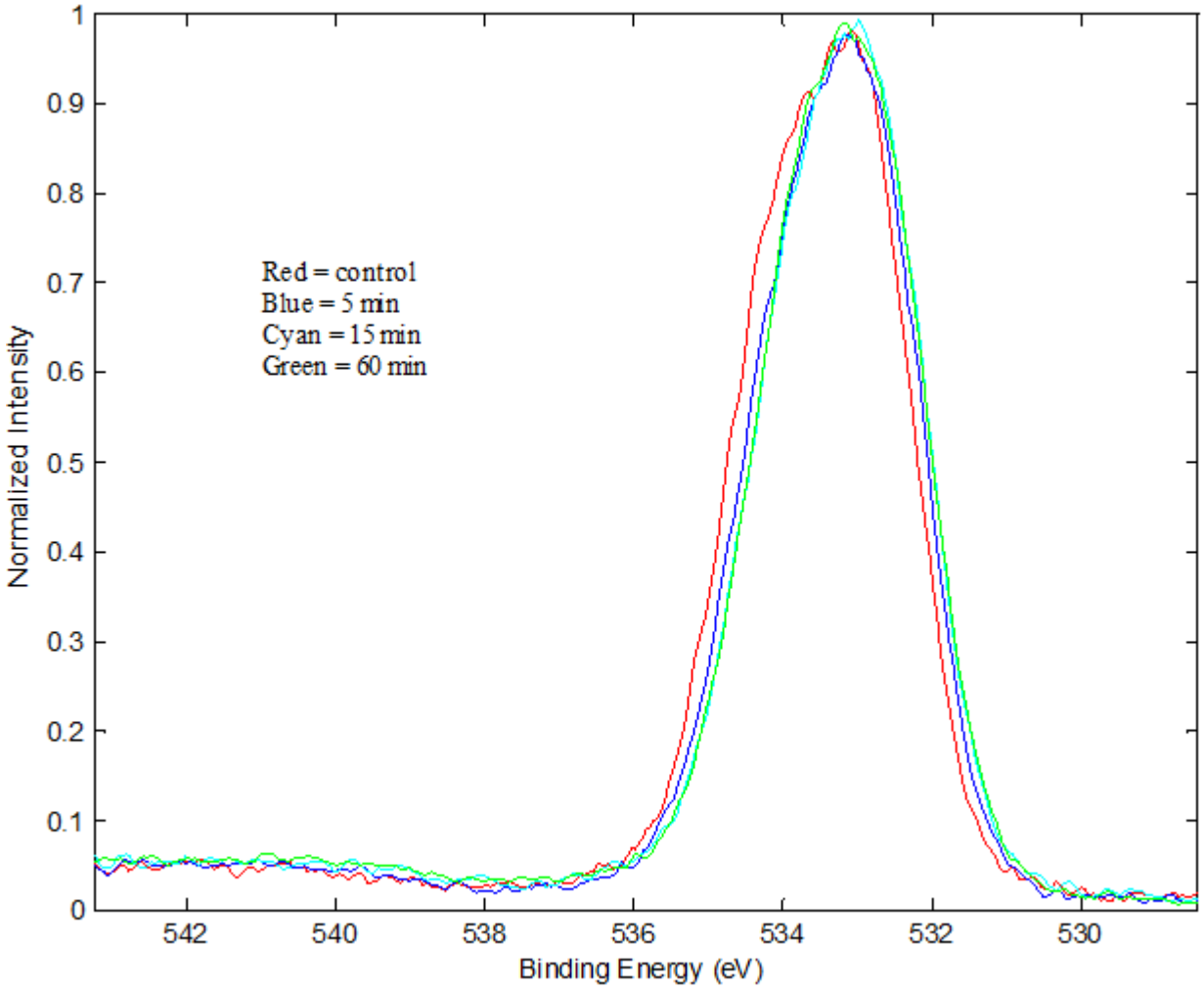

Figure 24: Overlapped O 1s Spectra for PAC Grafted Treated Polystyrene (Photo-oxidized using 184.9/253.7 nm irradiation)

Binding Energy (eV)	Control	5 min	15 min	60 min
532.5	22.2	34.1	39.9	41.8
533.4	51.7	43.4	34.0	34.6
534.5	26.1	22.5	26.1	23.7

Table 9: O 1s Peak Areas as Determined by Curve Fitting for PAC Grafted Treated Polystyrene (Photo-oxidized using 184.9/253.7 nm irradiation)

4.2 Surface Modification of Polystyrene using 253.7 nm Radiation

4.2.1 Surface Activation of Polystyrene by UV Photo-oxidation (253.7nm radiation)

4.2.1.1 Qualitative Analysis

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon and oxygen on the surface of every sample. Samples treated for 30 minutes or longer also contained nitrogen.

4.2.1.2 Quantitative Results

The results of the analyses are summarized in Table 10.

Sample	At% C	At% O	At% N
4PS0 control	98.8	1.2	0.0
5PS5 30 min	88.5	10.5	1.1
5PS15 60 min	80.6	18.4	1.0
5PS30 90 min	68.9	30.1	1.0
5PS60 120 min	64.8	33.8	1.4

Table 10: Results of the Quantitative XPS Analyses for the Polystyrene Films (Photo-oxidized by 253.7 nm irradiation).

The oxygen concentration (Fig 25) increased linearly for the first 90 minutes and then the amount of oxygen bonded to the surface increased slowly with treatment. The oxygen concentration began to plateau at well over 30 atomic percent of oxygen.

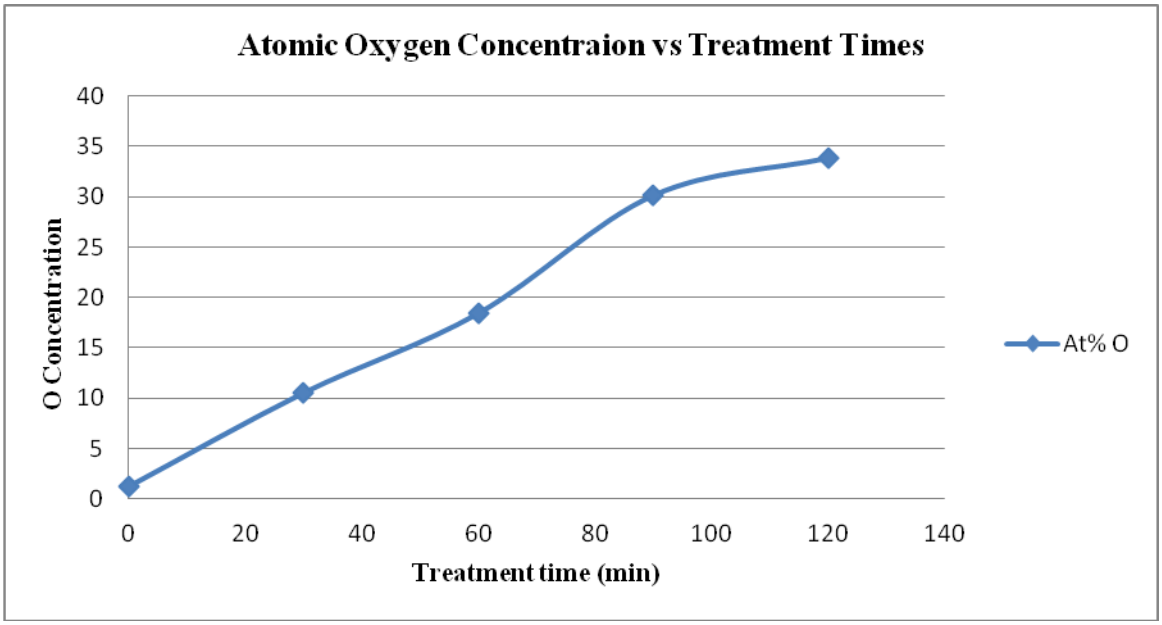

Figure 25: Atomic Oxygen Concentration vs. Treatment Times (Photo-oxidized by 253.7 nm irradiation).

4.2.1.3 Chemical State Analysis

There is increase in the concentration of carbon-oxygen species over the treatment times. Although the overlapped C 1s spectra (Figure 28) obtained for surface activation by 253.7nm radiation seems similar to the overlapped C 1s spectra for surface activation by 183.9nm/253.7nm (Figure 19), the surface change is slower for this technique.

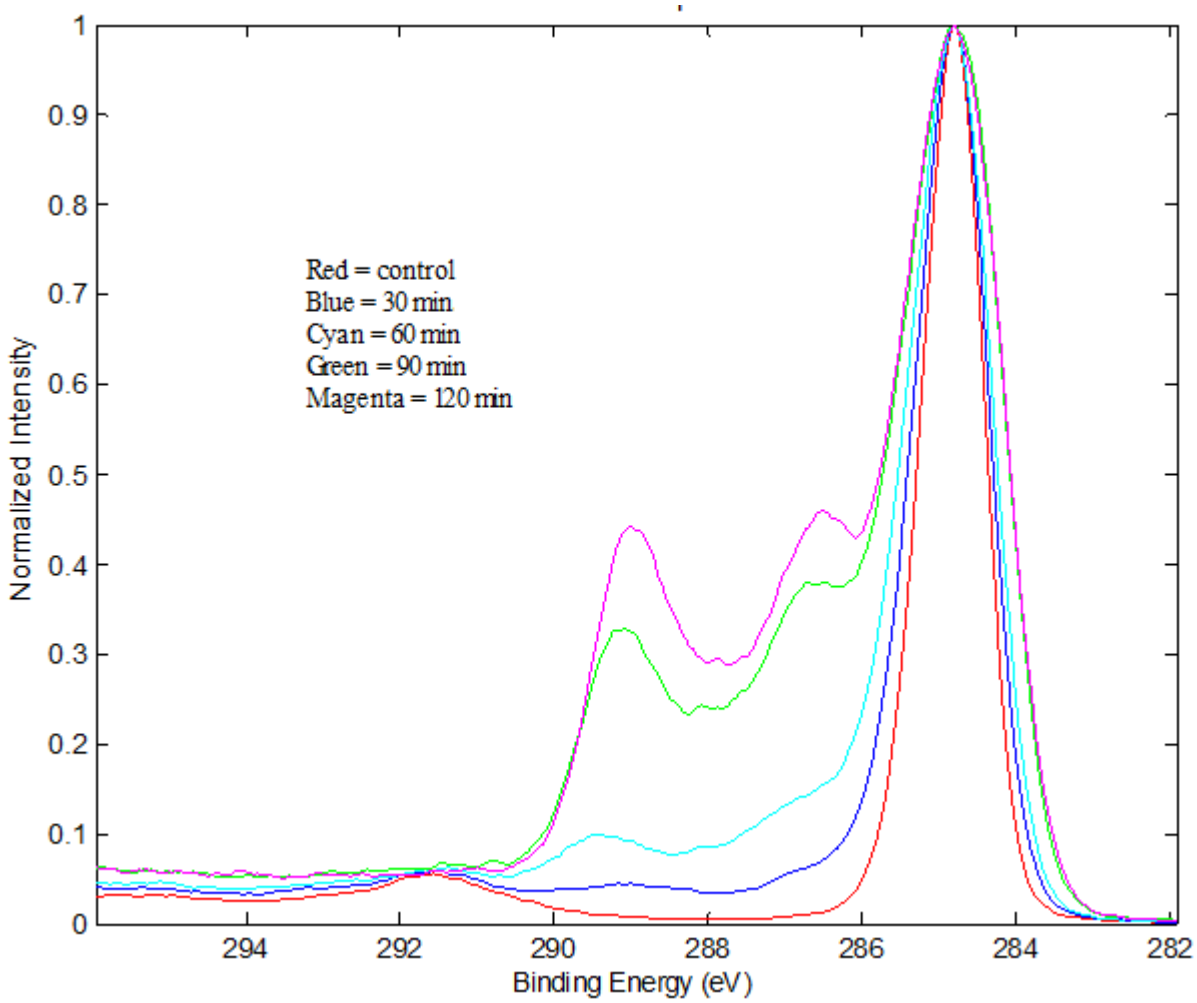

Figure 26: Overlapped C 1s Spectra for Control and Treated Polystyrene (Photo-oxidized by 253.7 nm irradiation).

The amount of carbon-oxygen bonding did not increase significantly for the first 30 minutes (Table 11). After treatment for 60 minutes C-O and C=O moieties became significant contributors to the spectra. After 90 to 120 minutes of treatment the acid/lactone contribution became significantly larger. This was evident in the spectra with the growth in intensity of the peak around 289 eV.

Binding Energy (eV)	Control	30 min	60 min	90 min	120 min
284.6	96.0	72.4	60.0	42.9	36.0
285.5	0.0	18.9	19.1	16.9	18.6
286.4	0.2	3.3	8.4	17.3	19.6
287.7	0.2	0.0	4.2	9.0	10.4
289.3	0.0	1.6	5.2	12.8	14.8
291.5	3.7	3.8	3.1	1.2	0.7

Table 11: Peak Areas for C 1s Peaks as Determined by Curve Fitting the C 1s Spectra (Photo-oxidized by 253.7 nm irradiation).

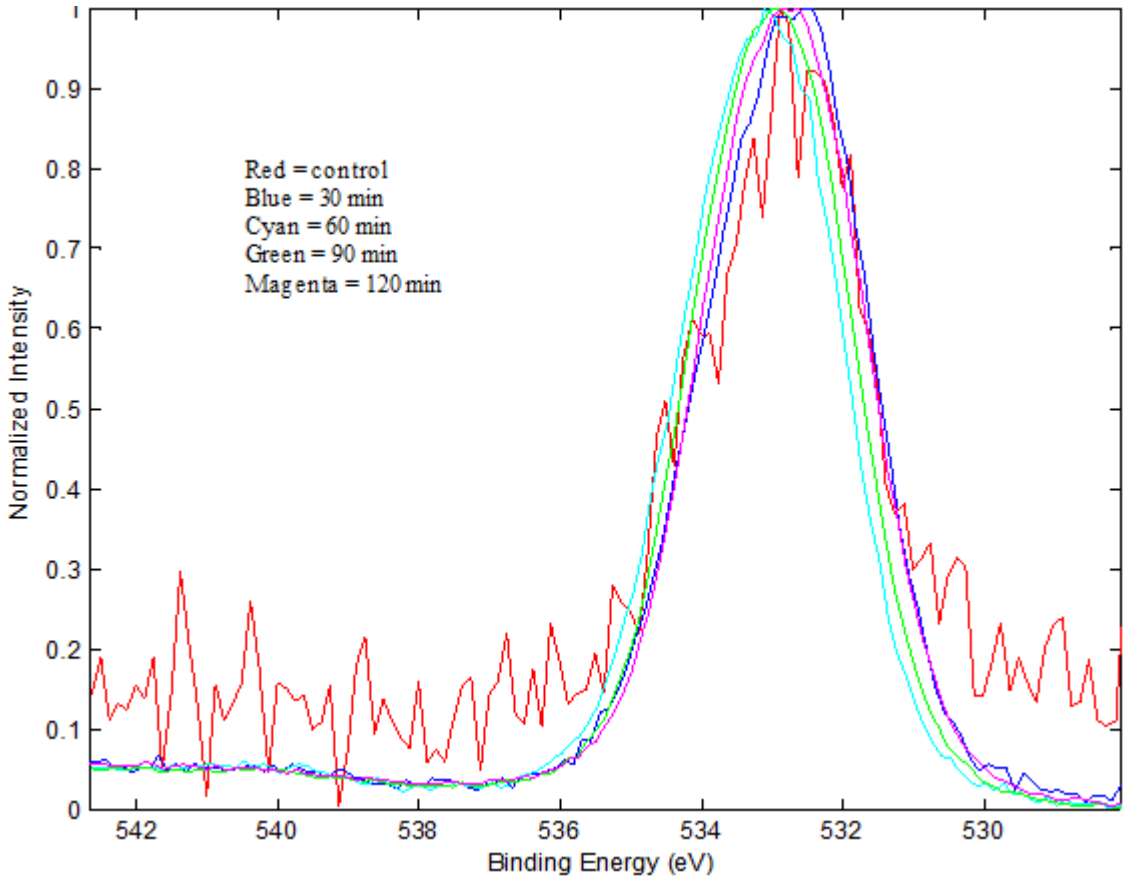

Figure 27: Overlapped O 1s Spectra for Control and Treated Polystyrene (Photo-oxidized by 253.7 nm irradiation).

Figure 27 shows the overlapped O 1s spectra for the samples. Due to the lack of energy resolution the O 1s spectra do not provide much additional information not already gained from the C 1s spectra. At short treatment times the O 1s spectra indicate the formation of hydroxyls and carbonyls (ketones). Longer treatment times resulted in an increase in the amount of esters, acid and lactone generated (Table 12).

Binding Energy (eV)	control	30 min	60 min	90 min	120 min
532.0	3.4	62.1	50.9	51.6	53.4
533.0	57.0	29.3	42.9	43.5	42.0
533.7	39.6	8.6	6.2	4.9	4.6

Table 12: O 1s Peak Areas as Determined by Curve Fitting for PS films (Photo-oxidized by 253.7 nm irradiation).

4.2.1.4 Contact Angle Measurement

The contact angle measurements are summarized in the Table 13.

Sample	Contact Angle
4PS0 control	84˚
5PS5 30 min	68˚
5PS15 60 min	51˚
5PS30 90 min	47˚
5PS60 120 min	43˚

Table 13: Contact Angle Measurements for 253.7nm treated Polystyrene Surface.

The plot of contact angle versus the treatment times is shown in Fig 28. The contact angle decreased gradually for the first 60 min and approached a plateau for higher treatment

times.

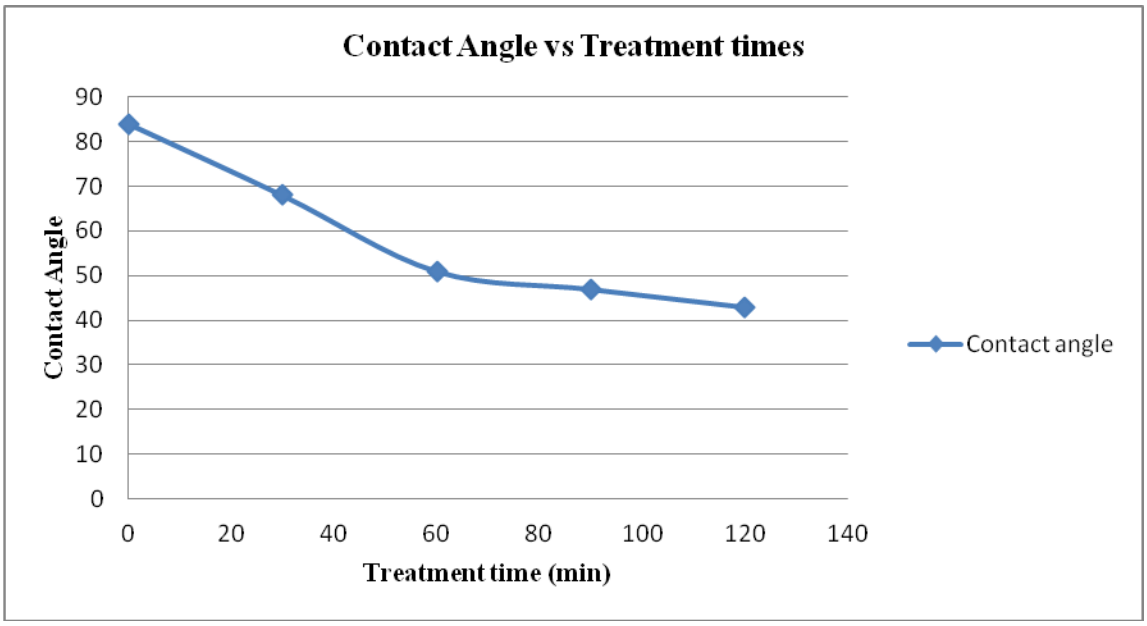

Figure 28 : Contact Angle vs. Treatment times for PS films (Photo-oxidized by 253.7 nm irradiation).

4.2.2 Grafting onto 253.7 nm surface treated Polystyrene

4.2.2.1 Qualitative Analysis

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon and oxygen on the surface of all five samples.

4.2.2.2 Quantitative Results

The results of the analyses are summarized in Table 14. Grafting onto samples treated for longer time showed an increase in the oxygen concentration. The control contained about 14.8 atomic percent of oxygen and the sample treated for 120 minutes contained 20.7 atomic percent of oxygen.

Sample	At% C	At% O
G-5PS0 control	85.18	14.82
G-5PS2 30 min	82.78	17.22
G-5PS5 60 min	82.74	17.26
G-5PS15 90 min	79.86	20.14
G-5PS60 120 min	79.35	20.65

Table 14: Results of the Quantitative XPS Analyses for PAC Grafted Treated Polystyrene (Photo-oxidized using 253.7nm irradiation).

4.2.2.3 Chemical State Analysis

Figure 29 shows the overlapped C 1s spectra obtained from a control and samples treated for 30, 60, 90 and 120 minutes. The principal peak at about 285 eV is due to alkyl and aromatic carbon-carbon bonding while peaks with binding energies greater than 285 eV are due to carbon-oxygen bonding. The peak due to $\Pi \rightarrow \Pi^*$ energy loss satellite became weaker after treatment of the polystyrene. This is indicative of a loss of phenyl groups from the surface. The relative growth in the peak at 289.3 eV is due to an increase in the amount of grafted PAC.

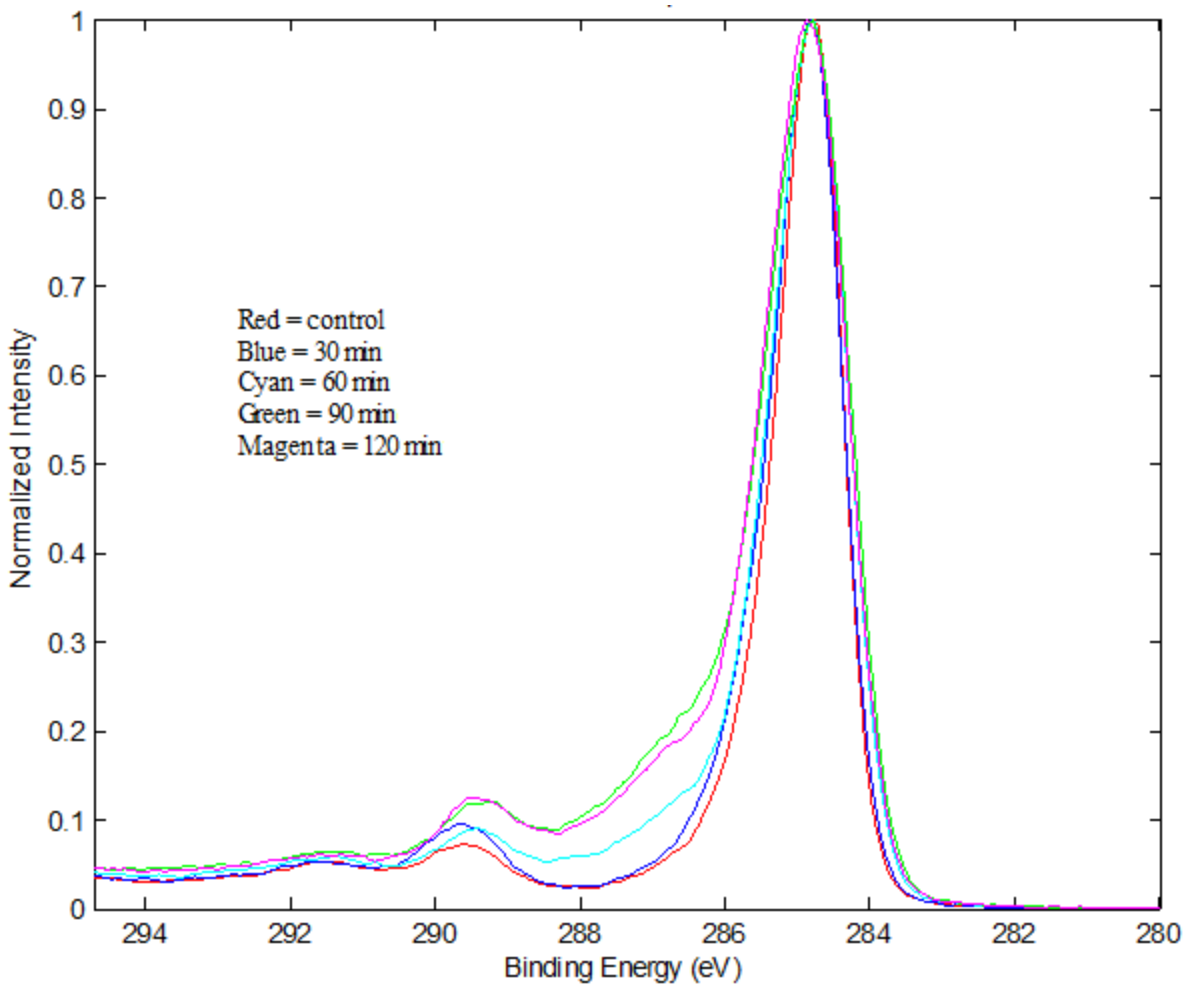

Figure 29: Overlapped C 1s Spectra for PAC Grafted Treated Polystyrene (Photo-oxidized using 253.7nm irradiation)

The results of the curve fitting for the C 1s peaks are summarized in Table 15. The major contributors to the C 1s spectra are the aromatic carbons. This suggests the oxidized polystyrene surface is not coated uniformly. The peak at 289.3 eV is due to the carboxyl group. The samples exhibit weak peaks due to acid. This indicates some PAC is present on the surface. The amount of carbon-carbon bonding due to the aromatic ring decreased as evidenced by the significant decrease in the energy loss structure associated with the $\Pi \rightarrow \Pi^*$ transition.

Binding Energy (eV)	0 min	30 min	60 min	90 min	120 min
284.6	69.5	68.4	73.2	60.5	60.7
285.2	21.6	21.1	13.0	16.1	18.0
286.4	2.5	2.6	6.3	11.1	9.5
287.7	0.0	0.0	0.0	5.1	4.4
289.3	3.7	5.5	5.6	5.0	5.6
291.5	2.8	2.4	1.9	2.3	1.8

Table 15: Peak Areas for C 1s Peaks as Determined by Curve Fitting the C 1s Spectra for PAC Grafted Treated Polystyrene (Photo-oxidized using 253.7nm irradiation)

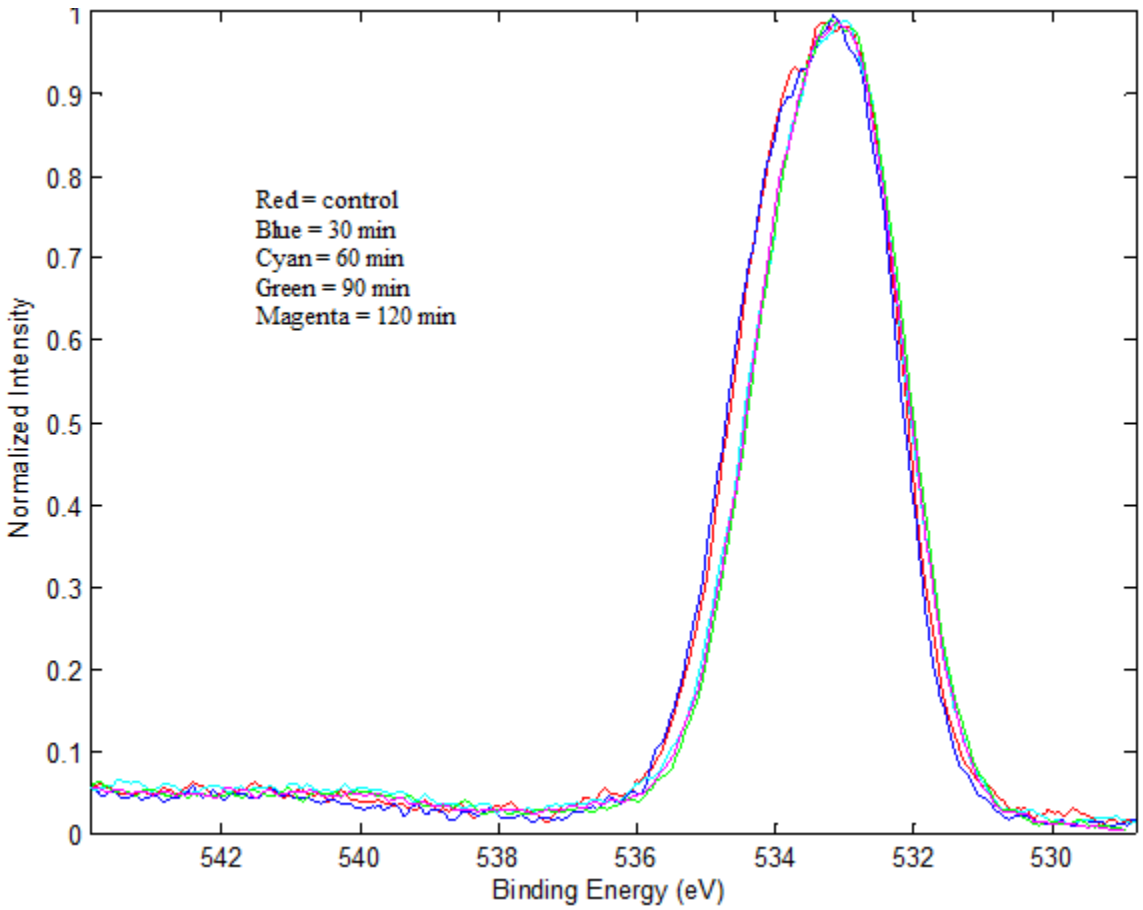

Figure 30: Overlapped O 1s Spectra for PAC Grafted Treated Polystyrene (Photo-oxidized using 253.7nm irradiation)

Figure 30 shows the overlapped O 1s spectra for the control and samples treated for 30, 60, 90 and 120 minutes. The spectra formed broad Gaussian peaks that made it difficult to extract information concerning the carbon-oxygen bonding. Due to the lack of energy resolution the O 1s spectra did not provide much additional information not already gained from the C 1s spectra. If only PAC was present the two O 1s peaks would have identical intensities. The low binding energy peak is more intense then the high binding energy peak. This is due to exposed oxidized polystyrene that is not grafted with PAC.

Binding Energy (eV)	control	30 min	60 min	90 min	120 min
532.5	40.0	39.2	36.7	40.8	41.3
533.4	29.2	30.7	36.7	35.3	35.1
534.5	30.8	30.1	26.6	24.0	23.7

Table 16: O 1s Peak Areas as Determined by Curve Fitting for PAC Grafted Treated Polystyrene (Photo-oxidized using 253.7nm irradiation)

4.3 Surface Modification of Polystyrene by Ozone

4.3.1 Surface Activation of Polystyrene by Ozone

4.3.1.1 Qualitative Analysis

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon and oxygen on the surface of every sample.

4.3.1.2 Quantitative Results

Quantitative analyses were obtained for the samples. The results of the analyses are summarized in Table 17.

Sample	At% C	At% O
2OP0 control	97.7	2.3
2OP1 110 min	92.2	7.8
2OP1 150 min	90.6	9.4
2OP1 210 min	89.4	10.6
2OP1 300 min	81.8	18.2
2OP1 360 min	81.7	18.3

Table 17: Results of the Quantitative XPS Analyses for PS films surface treated by Ozone.

The concentration of oxygen as a function of treatment time is shown in the plot below. The oxygen concentration reaches saturation after treatment for 300 minutes (Fig. 31).

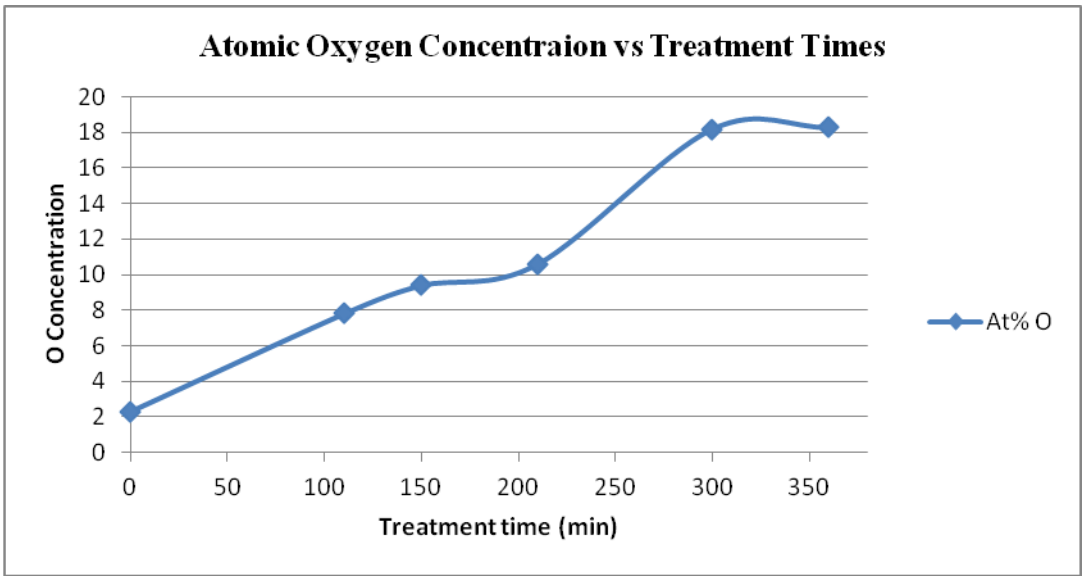

Figure 31: Atomic Oxygen Concentration vs. Treatment Times for PS films surface treated by Ozone.

4.3.1.3 Chemical State Analysis

Figure 32 shows the overlapped C 1s spectra obtained from the control and treated samples. The principal peak at 285 eV is due to carbon-carbon bonding. The manifold of peaks

with binding energies greater than 285 eV are due to carbon-oxygen bonding. The peak due to Π→Π* energy loss satellite becomes weaker after treatment of the polystyrene. This is indicative of oxidation of the phenyl ring. In order to determine the chemical species present on the surface the C 1s and O1s peaks were curve fit.

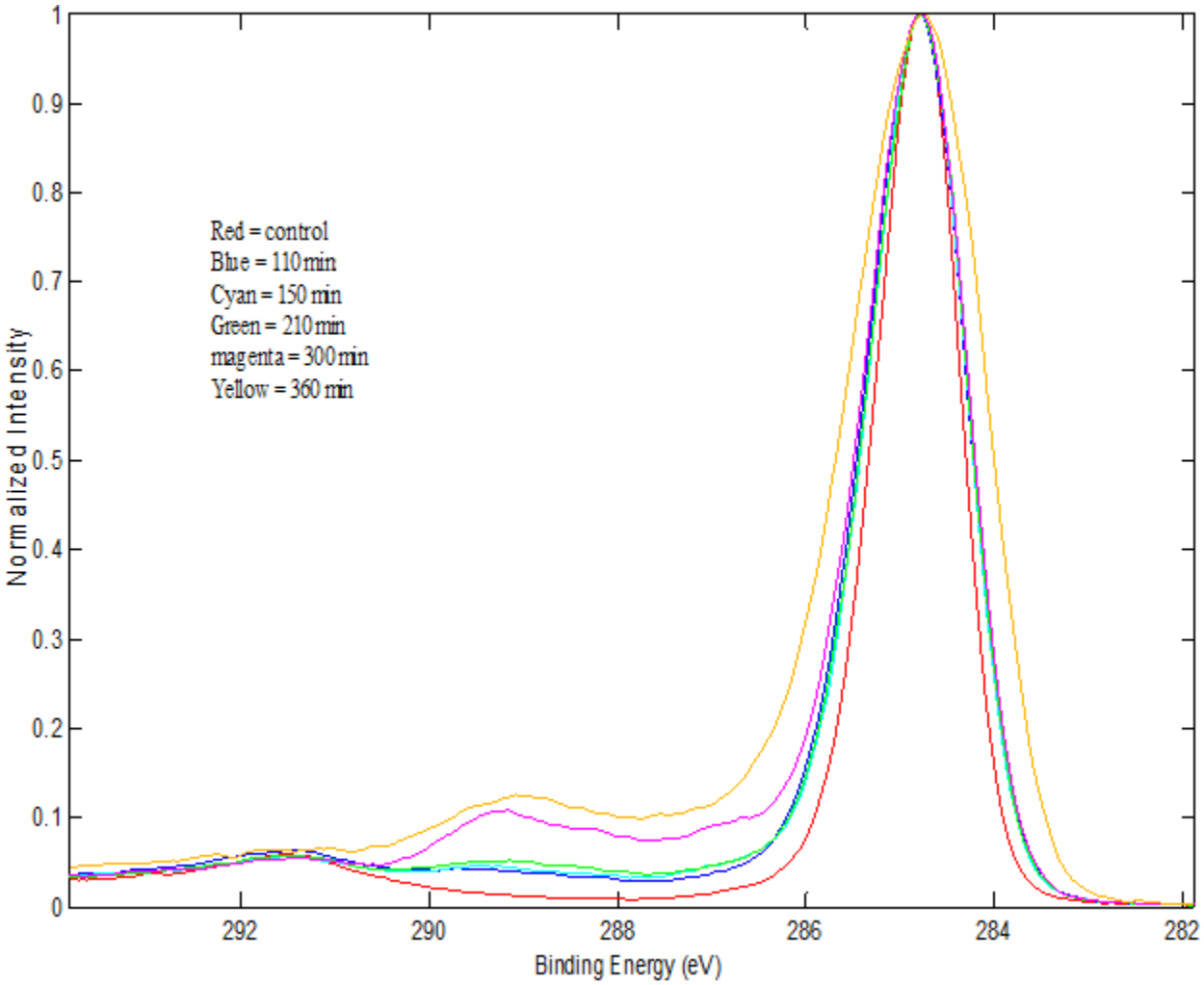

Figure 32: Overlapped C 1s Spectra for Control PS films surface treated by Ozone radiation.

The results of the curve fitting for the C 1s peaks are summarized in Table 18. The possible species that are the origins of the peaks are identified in Table 3. The major contributors to the C 1s spectra are the aromatic carbons. The amount of carbon-oxygen bonding increased almost linearly until it reached a plateau after 300 minutes of treatment. Ozone treatment is not

aggressive as it took about 3 hours of exposure to reach an oxygen concentration of 10 atomic percent. After 300 minutes of exposure to ozone the surface was not highly oxidized. The amount of acid groups accounts for about 6% of the carbon signal. There was also not a large portion of carbonyl carbon atoms as ketones. Most of the carbon atoms were singly bonded to carbon.

Binding Energy (eV)	Control	110 min	150 min	210 min	300 min	360 min
284.6	96.0	86.8	84.8	81.4	70.9	60.7
285.5	0.0	8.6	9.2	10.9	12.8	20.5
286.4	0.2	0.5	1.8	2.7	5.8	6.6
287.7	0.2	0.0	1.2	1.2	2.8	3.9
289.3	0.0	0.7	0.3	1.1	5.9	6.7
291.5	3.7	3.3	2.8	2.7	1.9	1.6

Table 18: Peak Areas for C 1s Peaks as Determined by Curve Fitting the C 1s Spectra for PS films surface treated by Ozone.

Figure 33 shows the overlapped O 1s spectra for the samples. The spectra are presented as raw data to show the relative increase in the intensity of the O 1s peak as a function of treatment time. At short treatment times the O 1s spectra indicate the formation of hydroxyls and carbonyls (ketones). Longer treatment times resulted in an increase in the amount of esters, acid and lactone generated.

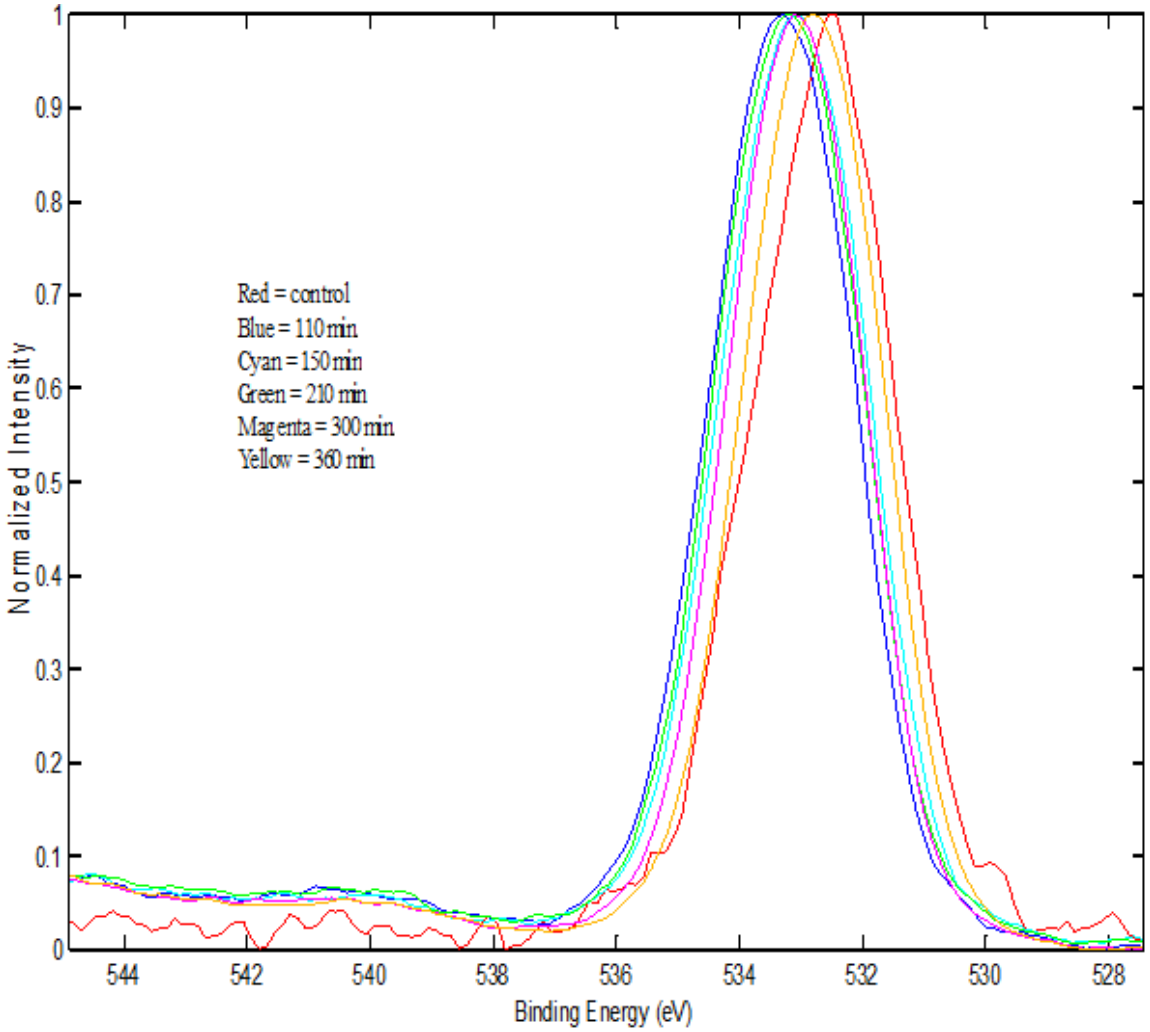

Figure 33: Overlapped O 1s Spectra for Control and for PS films for PS films surface treated by Ozone radiation.

Binding Energy (eV)	Control	110 min	150 min	210 min	300 min	360 min
532.0	27.1	28.5	32.4	31.1	32.9	40.4
533.0	46.2	40.9	36.1	34.1	34.5	30.6
533.7	26.6	30.6	31.5	34.8	32.6	29.0

Table 19: O 1s Peak Areas as Determined by Curve Fitting

4.3.2 Grafting onto Ozone treated Polystyrene

4.3.2.1 Qualitative Analysis

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon and oxygen on the surface of all six samples.

4.3.2.2 Quantitative Results

Quantitative analyses were obtained for the samples. The results of the analyses are summarized in Table 20. Treatment for longer time did not affect the oxygen concentration. The control contained the highest concentration of oxygen about 21 atomic percent of oxygen. The long term treated polystyrene contained between 15 and 17 atomic percent of oxygen.

Sample	At% C	At% O
G-2OP0 control	78.91	21.09
G-2OP1 110 min	83.90	15.10
G-2OP2 150 min	83.75	16.25
G-2OP3 210 min	84.42	15.58
G-2OP4 300 min	83.23	16.77
G-2OP5 360 min	84.57	15.43

Table 20: Results of the Quantitative XPS Analyses for PAC Grafted Treated Polystyrene (Surface treated by Ozone)

4.3.2.3 Chemical State Analysis

Figure 18 illustrates the C 1s spectrum for the polystyrene control and Figure 22 illustrates the C 1s spectrum for the PAC control. The energy loss structure associated with the Π→Π* transition of polystyrene is evident at about 291.5 eV Figure 34 shows the overlapped C 1s spectra obtained from a control and samples treated for 110, 150, 210, 300 and 360 minutes. The principal peak at about 285 eV is due to alkyl and aromatic carbon-carbon bonding. Peaks

with binding energies greater than 285 eV are due to carbon-oxygen bonding. The peak due to Π→Π* energy loss satellite did not change with treatment of the polystyrene. This indicates phenyl groups on the surface were not destroyed by treatment with ozone. In order to determine the chemical species present on the surface the C 1s and O1s peaks were curve fit. The peak at 289.3 eV is due grafted PAC. The most PAC was detected for the control. The area for the peak at 289.3 eV does not change with treatment time. Treatment of polystyrene with UV radiation resulted in a peak in the 287 eV range, probably due to the carbonyl moiety. This peak was absent in this series of samples treated with ozone.

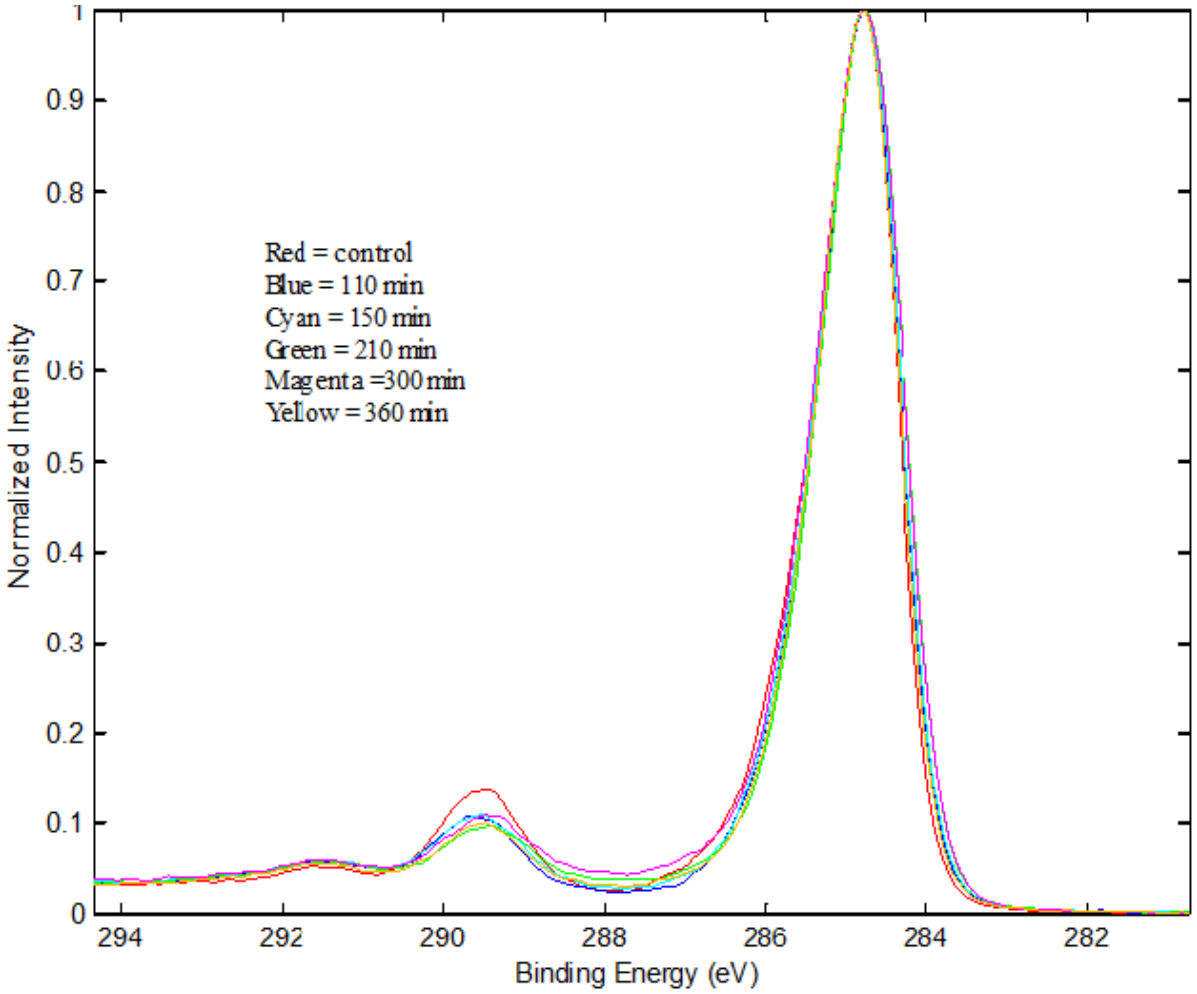

Figure 34: Overlapped C 1s Spectra for PAC Grafted Treated Polystyrene (Surface treated by Ozone radiation)

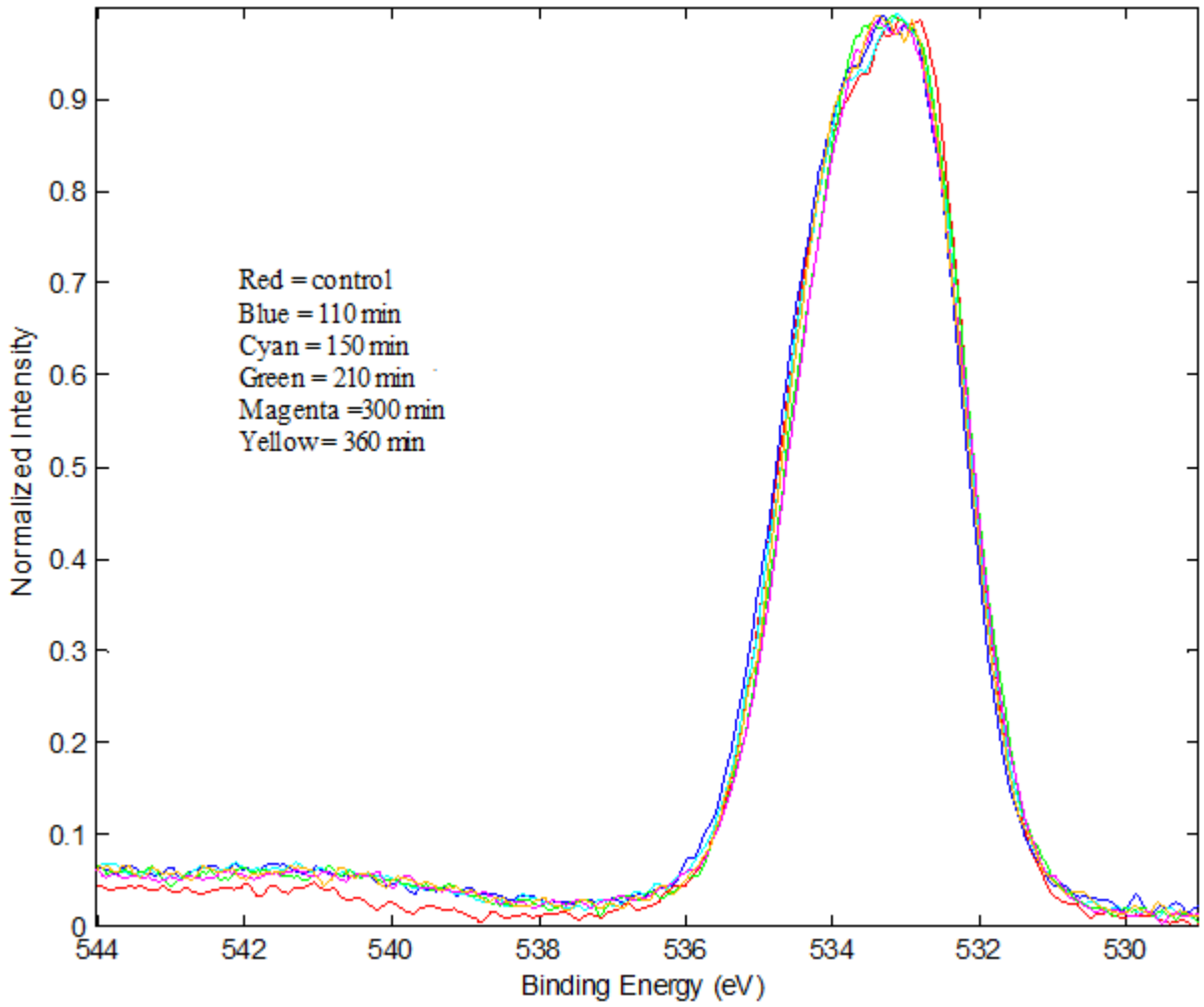

Figure 35: Overlapped O 1s Spectra for PAC Grafted Treated Polystyrene (Surface treated by Ozone)

The results of the curve fitting for the C 1s peaks are summarized in Table 21. Possible species that are the origins of the peaks are identified in Table 3. The major contributors to the C 1s spectra were the aromatic carbons. This suggests the oxidized polystyrene surface is not coated uniformly. The peak at 289.3 eV is due to the carboxyl group. The samples exhibit weak peaks due to acid. This indicates some PAC is present on the surface.

Binding Energy (eV)	0 min	100 min	150 min	210 min	300 min	360 min
284.6	59.0	66.6	66.0	72.5	68.7	68.7
285.2	28.2	23.1	23.5	16.1	19.7	20.6
286.4	2.7	1.3	1.6	1.5	1.9	1.4
287.7	0.0	0.0	0.0	0.0	0.0	0.0
289.3	8.5	6.2	6.3	6.8	7.4	6.5
291.5	1.6	2.8	2.6	3.0	2.5	2.9

Table 21: Peak Areas for C 1s Peaks as Determined by Curve Fitting the C 1s Spectra for PAC Grafted Treated Polystyrene (Surface treated by Ozone)

Figure 35 shows the overlapped O 1s spectra for the control and samples treated for 110, 150, 210, 300 and 360 minutes. The spectra formed broad Gaussian peaks that made it difficult to extract information concerning the carbon-oxygen bonding. Curve fittings were performed and the results are summarized in Table 22. Literature values[31] for the various species are summarized in Table 5. Due to the lack of energy resolution the O 1s spectra do not provide much additional information not already gained from the C 1s spectra. If only PAC was present the two O 1s peaks would have identical intensities. The low binding energy peak is more intense then the high binding energy peak. This is due to exposed oxidized polystyrene that is not grafted with PAC.

Binding Energy (eV)	Control	110 min	150 min	210 min	300 min	360 min
532.5	41.3	42.0	37.8	38.2	36.5	39.5
533.4	26.9	30.2	29.7	32.5	34.0	29.5
534.4	31.8	27.8	32.5	29.2	29.6	31.0

Table 22: O 1s Peak Areas as Determined by Curve Fitting for PAC Grafted Treated Polystyrene (Surface treated by Ozone).

4.4 Surface Modification of Nafion

4.4.1 Cleaning

5 control samples were cleaned to remove surface contamination exhibiting carbon-carbon and carbon-oxygen bonding by the 3 step process as described in Section 3.1.2.

4.4.1.1 Qualitative Results for Cleaned Control Samples

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon, fluorine, oxygen and sulfur on the surface of every sample. Control S3 was contaminated with calcium and nitrogen.

4.4.1.2 Quantitative Results for Cleaned Control Samples

The results of the analyses are summarized in Table 23. These quantitative analysis results for the cleaned Nafion samples are in good agreement with the values quoted by M. Schulze et al.[32] Sample S3 was contaminated possibly during the handling or the testing process. The results for the other samples closely matched with the calculated atomic concentration (Table 23).

Control Samples	At% C	At% O	At% F	At% S	At% N	At% Ca
S1	34.8	8.1	55.8	1.4	0.0	0.0
S2	35.0	7.0	56.7	1.3	0.0	0.0
S3	26.4	31.6	29.6	8.5	1.5	2.4
S4	35.2	6.6	57.1	1.1	0.0	0.0
S5	32.8	9.5	56.1	1.7	0.0	0.0
Stoichiometric calculation	28.1	15.6	53.1	3.1	0.0	0.0

Table 23: Results of the Quantitative XPS Analyses for the cleaned Nafion-117 Films

XPS cannot detect hydrogen due to its low photoionization cross section.

4.4.1.3 Chemical State Results

The overlapped C 1s spectra for the samples are illustrated below in Figure 36. There are two distinct groups of peaks in the C 1s spectrum, one at low binding energy and one at high binding energy. The peaks at low binding energy are due to carbon-carbon and carbon-oxygen bonding environments. The group of peaks at high binding arises from carbon bonding to fluorine. The C 1s binding energies are summarized in Table 24. Peak assignments were made by reference to the literature.[31]

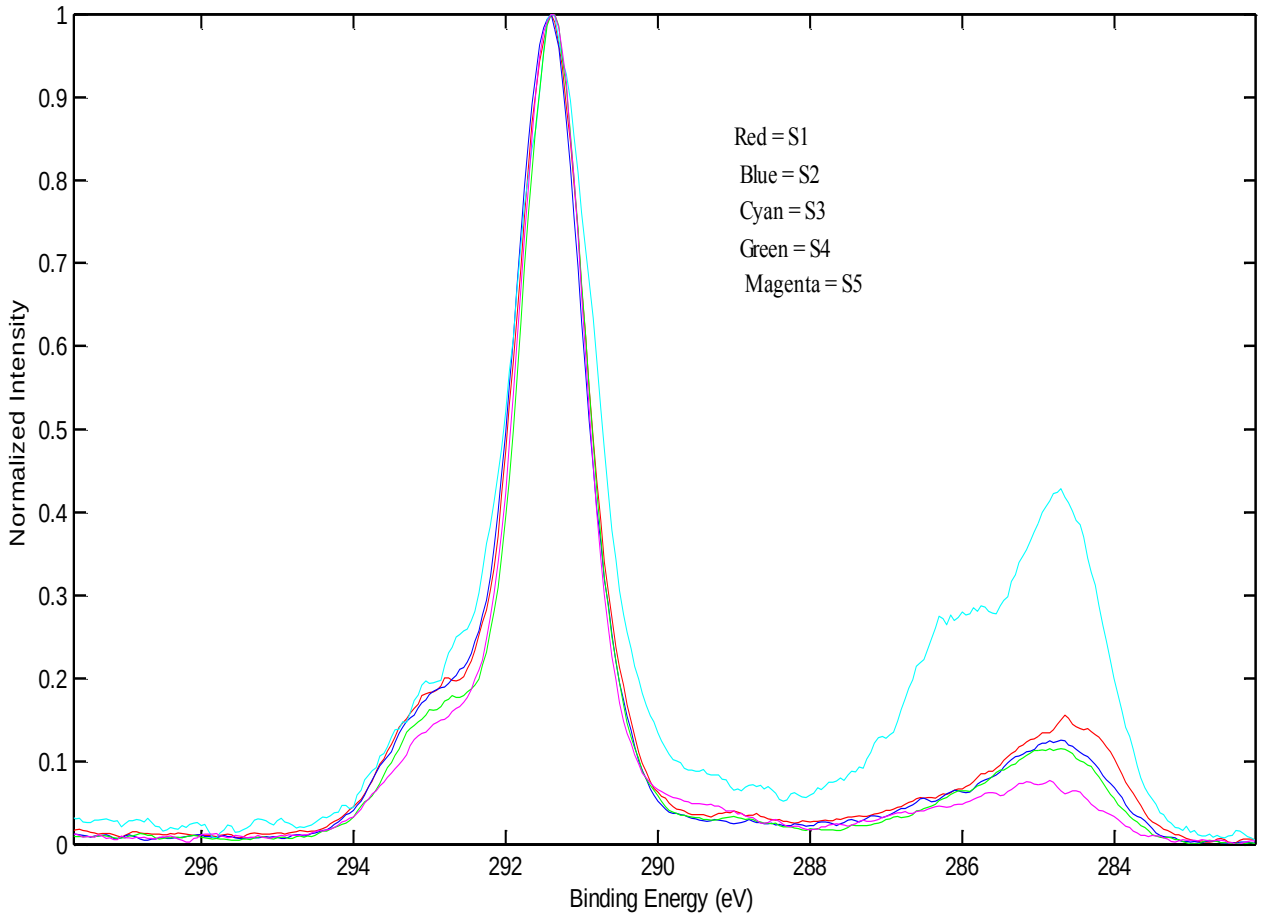

Figure 36: Overlapped C 1s Spectra for the cleaned Nafion-117 Film Samples

Species	Binding Energy (eV)
C-C	284.7
O-C-C* ‖ O	285.4
C*-O-C=O	286.2
O=C-O	289.3
CF	289.2
CF_2	291.8
CF_3	293.0

Table 24: C 1s Binding Energies for the Cleaned Nafion Samples[31]

The O 1s spectra show two distinct peaks with evidence of at least a third peak that lies between the low and high binding energy peaks that can be resolved (Fig. 37). The low binding energy peak is due to the sulfonic acid group. The high binding energy peak is due to oxygen bonded to the CF and CF_2 moieties. The peak(s) that lies between these peaks are due to the O-C=O moiety. The O 1s binding energies and results of the curve fittings are presented in Tables 25 and 28 respectively.

Species	Binding Energy (eV)
O-C=O (Composite)	532.7
Sulfonic acid	533.4
CF-O*-CF_2	535.1

Table 25: O 1s Binding Energies for the Cleaned Nafion Samples[31]

The overlapped S 2p spectra illustrated below show the presence of at least two sulfur peaks. The intense S 2p peak at high binding energy is due to sulfonic acid. The low binding energy peak is due to an S-O moiety bonded to an organic species. This is probably a decomposition product of Nafion. The S 2p binding energies are summarized in Table 26 and the results of the curve fitting are reported in Table 27.

	S1	S2	S3	S4	S5
organoS-O_X	165.0	164.6	164.9	164.9	165.1
Sulfonic acid	169.4	168.9	169.1	169.5	169.5

Table 26: S2p Binding Energies for the Cleaned Nafion Films

	S1	S2	S3	S4	S5
C-C	9.4	7.9	18.0	8.3	4.2
O-C-C* / F-C-C* ‖ O	5.9	5.5	9.7	4.8	4.6
C*-O-C=O	4.6	3.8	11.6	2.8	3.4
O=C-O	2.6	1.7	3.1	2.5	4.1
CF	12.6	13.0	5.3	6.7	8.5
CF_2	52.0	54.2	40.7	60.8	63.1
CF_3	13.0	14.0	11.6	14.0	12.1

Table 27: Results of the Curve Fitting for the C 1s Spectra of the Cleaned Nafion-117 Films

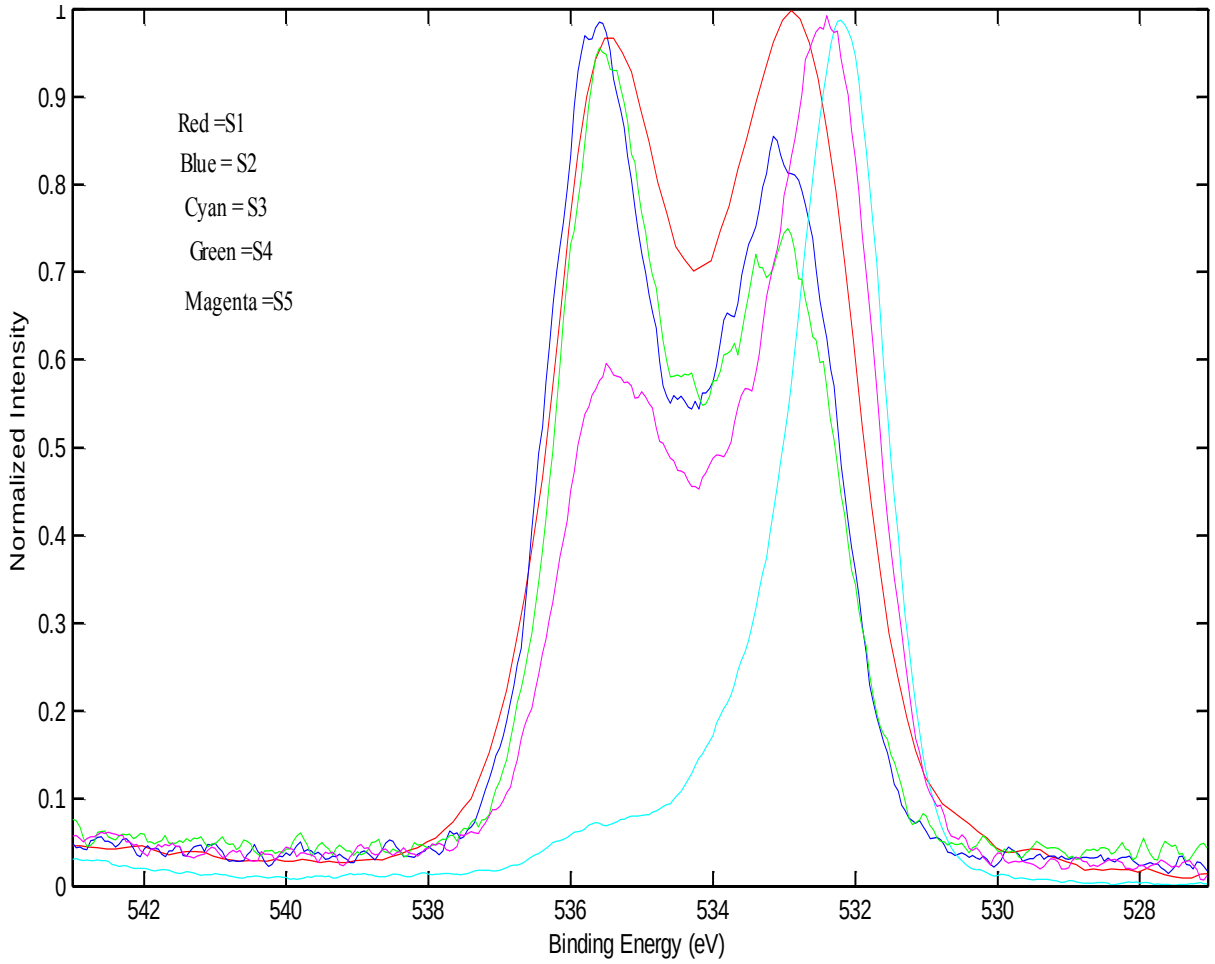

Figure 37: Overlapped O 1s Spectra for the Cleaned Nafion-117 Film Samples

	S1	S2	S3	S4	S5
Sulfonic acid	44.7	39.1	69.2	35.3	29.5
O-C=O	10.8	17.2	25.2	10.5	35.0
CF-O*-CF_2	44.5	43.8	5.7	54.2	35.5

Table 28: Results of the Curve Fitting for the O 1s Spectra of the Cleaned Nafion-117 Films

	S1	S2	S3	S4	S5
organoS-O_X	17.3	19.5	3.5	14.2	6.0
Sulfonic acid	82.7	80.5	96.5	85.8	94.0

Table 29: Results of the Curve Fitting for the S 2p Spectra of the Cleaned Nafion-117 Films

4.4.2 Surface Activation of Nafion with VUV Photo-oxidation

4.4.2.1 Qualitative Results

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon, fluorine, oxygen and sulfur on the surface of every sample.

4.4.2.2 Quantitative Results

The results of the analyses are summarized in Table 30. In general, an increase in treatment time resulted in an increase in the concentration of oxygen and a decrease in the concentration of carbon.

Sample	At% C	At% O	At% F	At% S
7N0 control	31.1	8.3	59.7	0.9
7N15 15 min	35.4	8.0	56.1	0.4
7N30 30 min	35.4	8.8	55.2	0.6
7N60 60 min	31.4	12.3	54.4	2.0

Table 30: Results of the Quantitative XPS Analyses for the VUV Photo-oxidized Nafion-117 Films

4.4.2.3 Chemical State Results

The overlapped C 1s spectra for the samples are illustrated below in Figure 38 and the overlapped O 1s spectra are shown in Figure 39. The peaks at low binding energy are due to carbon-carbon and carbon-oxygen bonding environments. The group of peaks at high binding

arises from carbon bonding to fluorine. The principal peak at high binding energy is assigned to the CF_2 moiety and the high binding energy shoulder at about 293 eV is attributed to the CF_3 moiety.

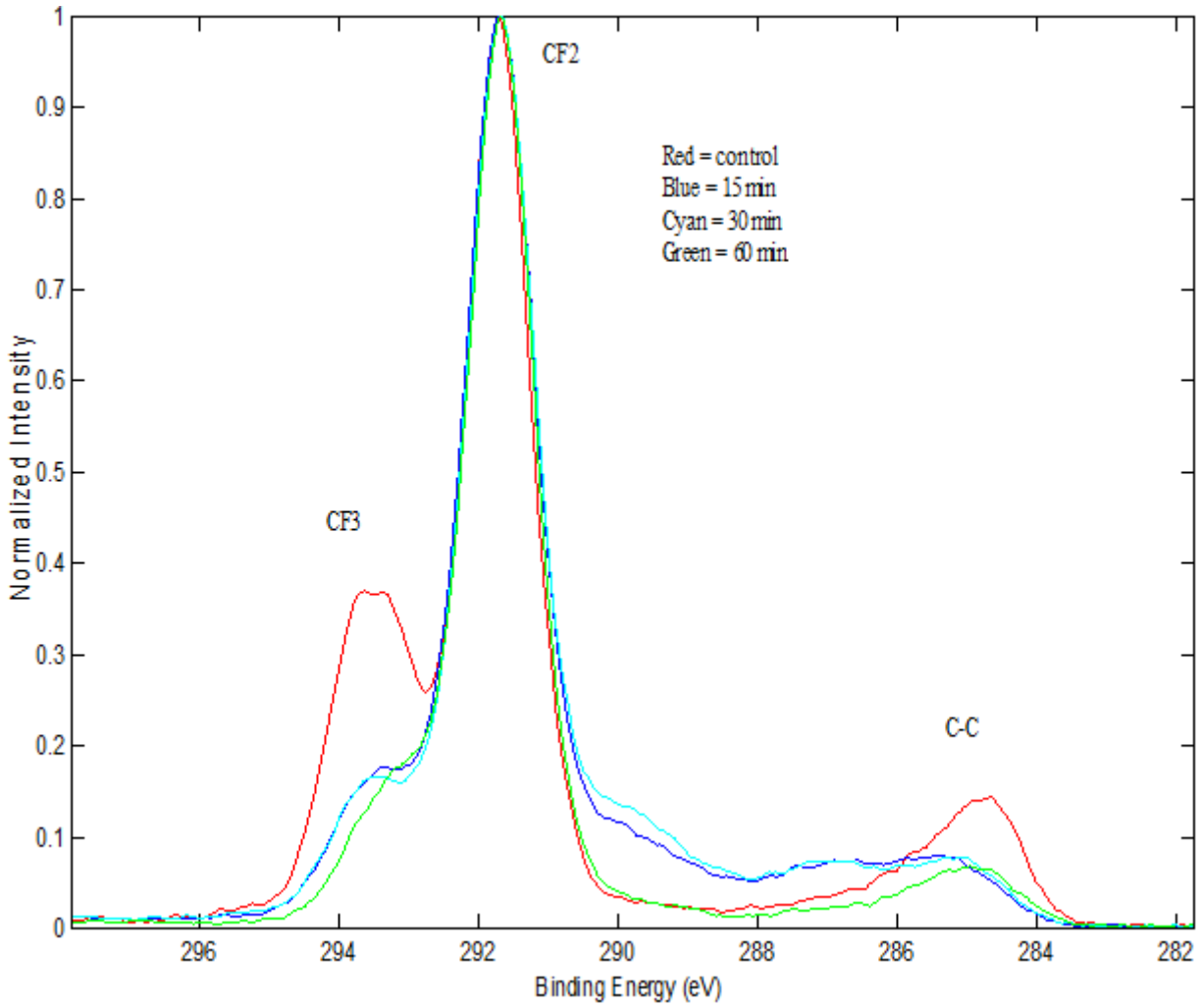

Figure 38: Overlapped C 1s Spectra for the VUV Photo-oxidized Nafion-117 Films

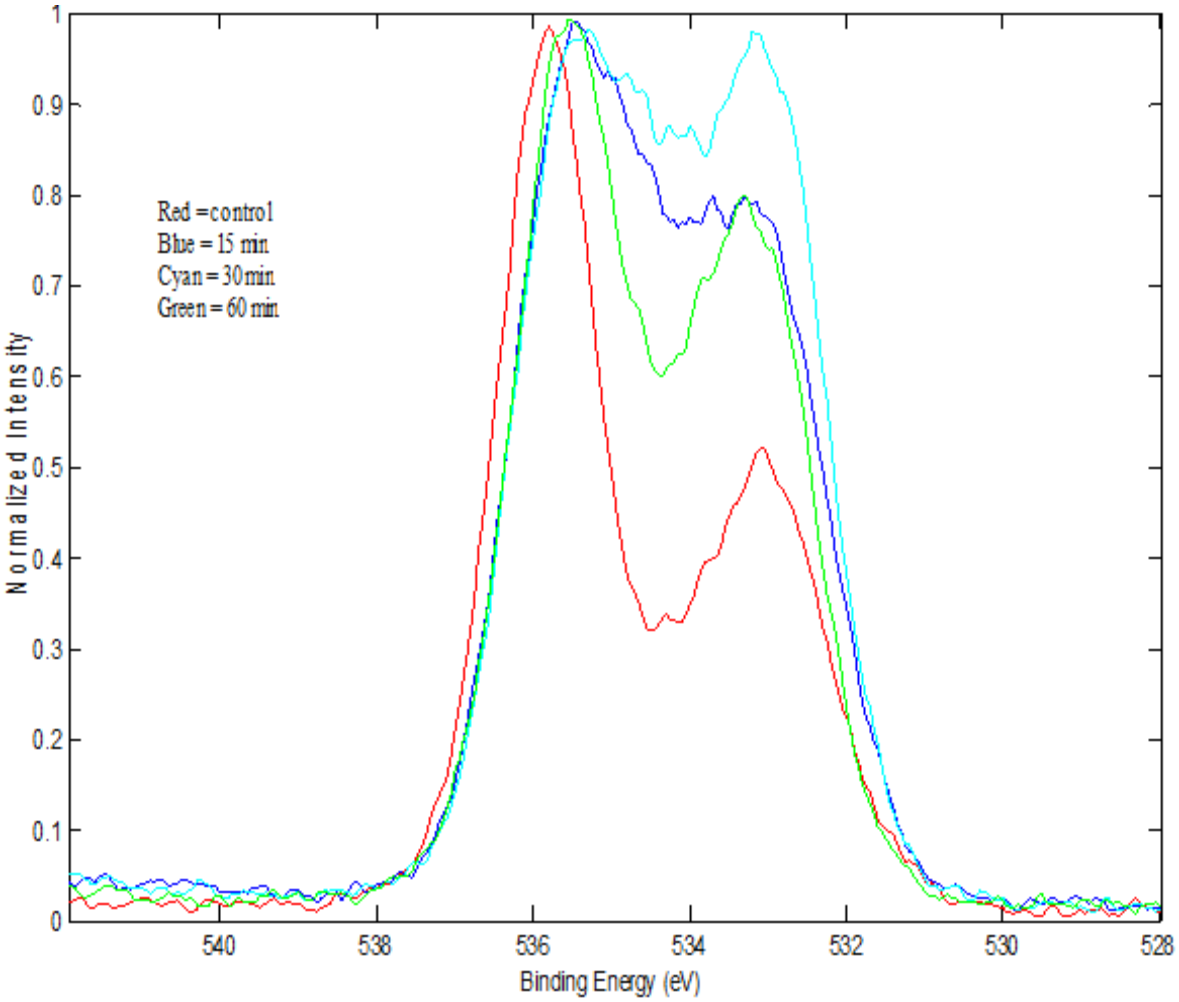

Figure 39: Overlapped O 1s Spectra for the VUV Photo-oxidized Nafion-117 Films

The C 1s binding energies are summarized in Table 24. Peak assignments were made by reference to the literature.[31]

The results of curve fitting the C 1s peaks for the samples are tabulated in Table 31. In general, the peaks due to carbon-carbon bonding and the CF_3 moiety decreased with the length of treatment. Peaks due to carbon-oxygen bonding became strong enough to contribute to the curve fitting. The contribution of the peak due to the CF_2 moiety did not change much with treatment.

The O 1s spectra exhibit a peak at about 535 eV and a second well defined peak at approximately 533 eV. The O 1s binding energies are summarized in Table 25. The peak at the

lowest binding energy is assigned to the oxygen atoms of the sulfonic acid group and carbon-oxygen bonding. The oxygen in the CF-O-CF_2 backbone of Nafion yields the strong O 1s peak at about 535 eV.

The curve fitting for the O 1s spectra employed two peaks to give a good fit. One peak is due to CF-O-CF_2, another due to the composite peak from the oxygen of the sulfonic acid group and carbon-oxygen bonding. Since the two peaks could not be resolved a more accurate curve fitting could not be made. For example, water of hydration is probably present and one or more carbon-oxygen moieties. In general, the curve fittings show a slight increase in carbon-oxygen bonding with treatment time, a decrease in the amount of oxygen due to the sulfonic acid group and finally a decrease in the CF-O-CF_2 moiety with increasing treatment time. The sample treated for 60 minutes did not fit the pattern.

Species	Control	15 min	30 min	60 min
C-C	7.3	7.1	6.6	3.0
O-C-C* ‖ O	1.6	3.9	4.2	1.9
C*-O-C=O	0.8	2.9	3.4	2.0
O=C-O	2.2	0.5	1.1	7.2
CF	3.5	8.9	10.2	2.6
CF_2	66.8	65.5	64.0	68.9
CF_3	17.9	11.2	10.5	14.5

Table 31: Results of the Curve Fitting for the C 1s Spectra for the VUV Photo-oxidized Nafion-117 Films

Species	Control	15 min	30 min	60 min
C-O composite + acid	40.4	49.6	50.6	63.5
CF-O*-CF2	59.7	50.4	49.4	36.6

Table 32: Results of the Curve Fitting for the O 1s Spectra for the VUV Photo-oxidized Nafion-117 Films

4.4.3 Grafting onto Activated Nafion

4.4.3.1 Qualitative Results

The elemental survey scans from 0 eV to 1000 eV binding energy detected carbon, fluorine, oxygen and sulfur on the surface of every sample.

4.4.3.2 Quantitative Results

Table 33 shows the XPS quantitative analysis results for pre-treated Nafion samples that were exposed to 0 - 60 min of VUV photo-oxidation and then grafted with acrylic acid, H_2C=CH-COOH. The data shows a decrease in F at% and an increase in C and O at% with VUV treatment time as expected when grafting poly(acrylic acid) to the modified Nafion substrate.

VUV Treatment time, Min	At% C	At% O	At% F	At% S	O/C	F/C	S/C
0	39.6	10.7	48.6	1.2	0.27	1.23	0.03
30	50.3	20.8	28.7	0.3	0.41	0.57	0.006
60	67.3	31.2	1.4	0.05	0.46	0.02	0.0007

Table 33: Results of the quantitative XPS analyses after 1.5 h of poly(acrylic acid) grafting to Nafion films treated with VUV photo-oxidation.

4.4.3.3 Chemical State Results

The overlapped C 1s spectra for the samples modified with 0, 0.5 and 1 h VUV photo-oxidation and then grafted with acrylic acid are shown in Fig. 40. The peaks at high binding

arise from carbon bonded to fluorine in Nafion while the peaks at low binding energy are due to carbon-carbon and carbon-oxygen bonding environments. The results of the curve fittings are summarized in Table 34. Initially a significant amount of carbon-fluorine bonding, due to Nafion, was observed. After 30 minutes of activation and then grafting, a significant amount of carbon-carbon and carbon-oxygen bonding was observed. After 60 minutes of activation, the surface exhibits a very low amount of carbon-fluorine bonding and the surface chemistry was dominated by carbon-carbon bonding due to the grafting of poly(acrylic acid).

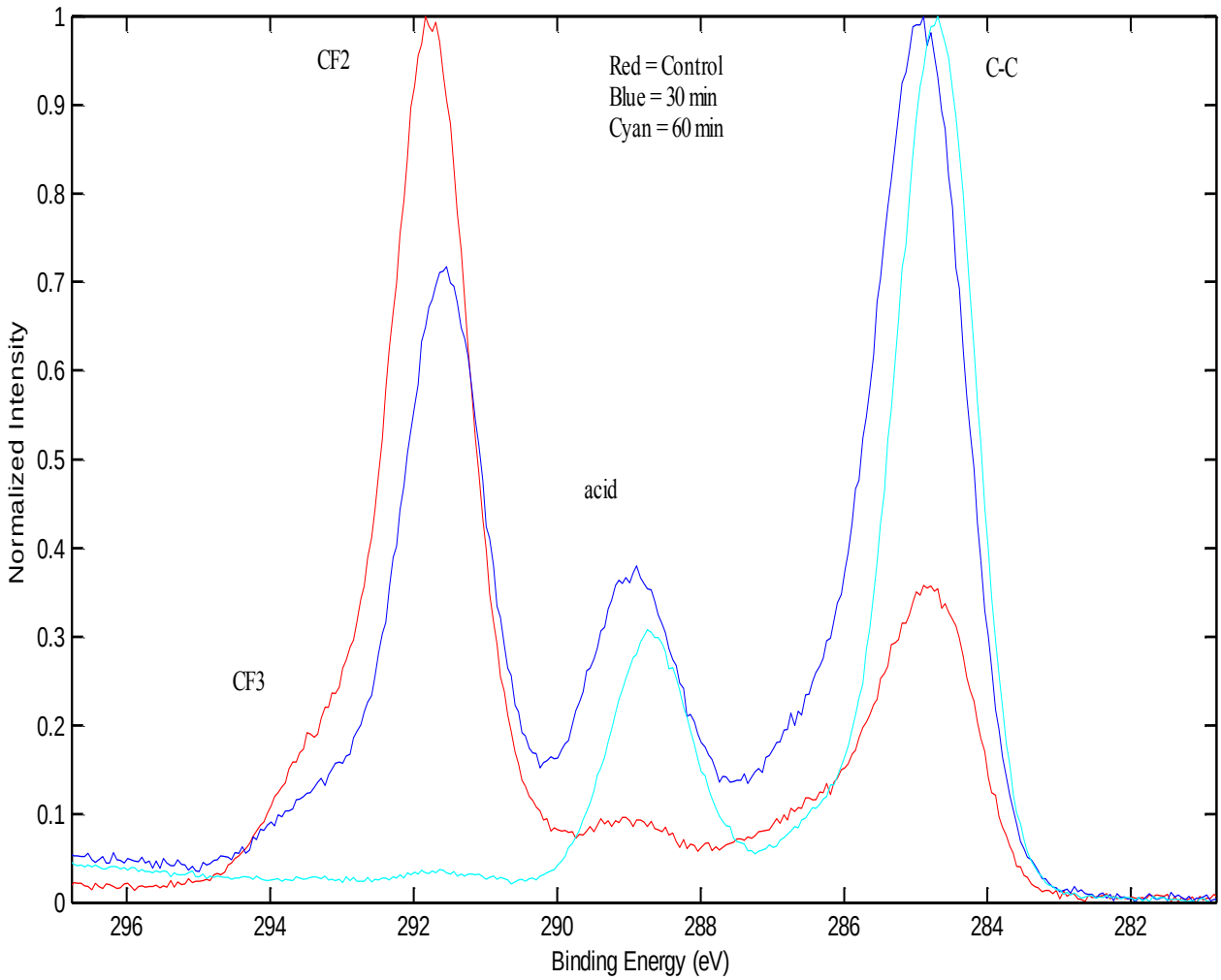

Figure 40: The overlapped C 1s spectra for the samples modified with 0, 0.5 and 1 h VUV photo-oxidation and then grafted with acrylic acid

Assignment	Binding Energy (eV)	0 h	0.5 h	1 h
C-C	284.6	20.7	41.6	73.2
C*-C=O | OH	285.8	4.7	6.5	5.0
C-O-C, C-OH	286.5	2.9	4.0	2.8
O-C=O	289.1	3.0	9.0	10.7
C-C*=O | OH	289.3	3.4	7.7	8.3
CF_2-CF_2	292.5	58.3	28.7	0.0
CF_3	293.8	7.1	2.8	0.0

Table 34: Results of the curve fittings of the C 1s spectra for poly(acrylic acid) grafted to VUV photo-oxidized Nafion-117 samples

The O 1s spectrum for the control where grafting was attempted (Fig. 41) shows two distinct peaks with evidence of at least a third peak that lies between the low and high binding energy peaks that could be resolved. The low binding energy peak is due to carbon-oxygen bonding. The sulfur concentration was too low for the sulfonic acid group to contribute significantly to the overall O 1s spectrum after 30 and 60 minutes of treatment. The high binding energy peak is due to oxygen bonded to CF moieties in Nafion. The O 1s binding energies and the results of the curve fittings are presented in Table 35**,** respectively, for the carbon-oxygen species. The O 1s spectra for the activated samples did not exhibit any energy resolved peaks to aid spectral interpretation and curve fitting. Oxygen due to Nafion could not be detected after activation for 60 minutes. Curve fitting shows the growth of a new low binding energy O 1s peak with treatment time. This peak arises from the loss of hydrogen from the carboxyl group.

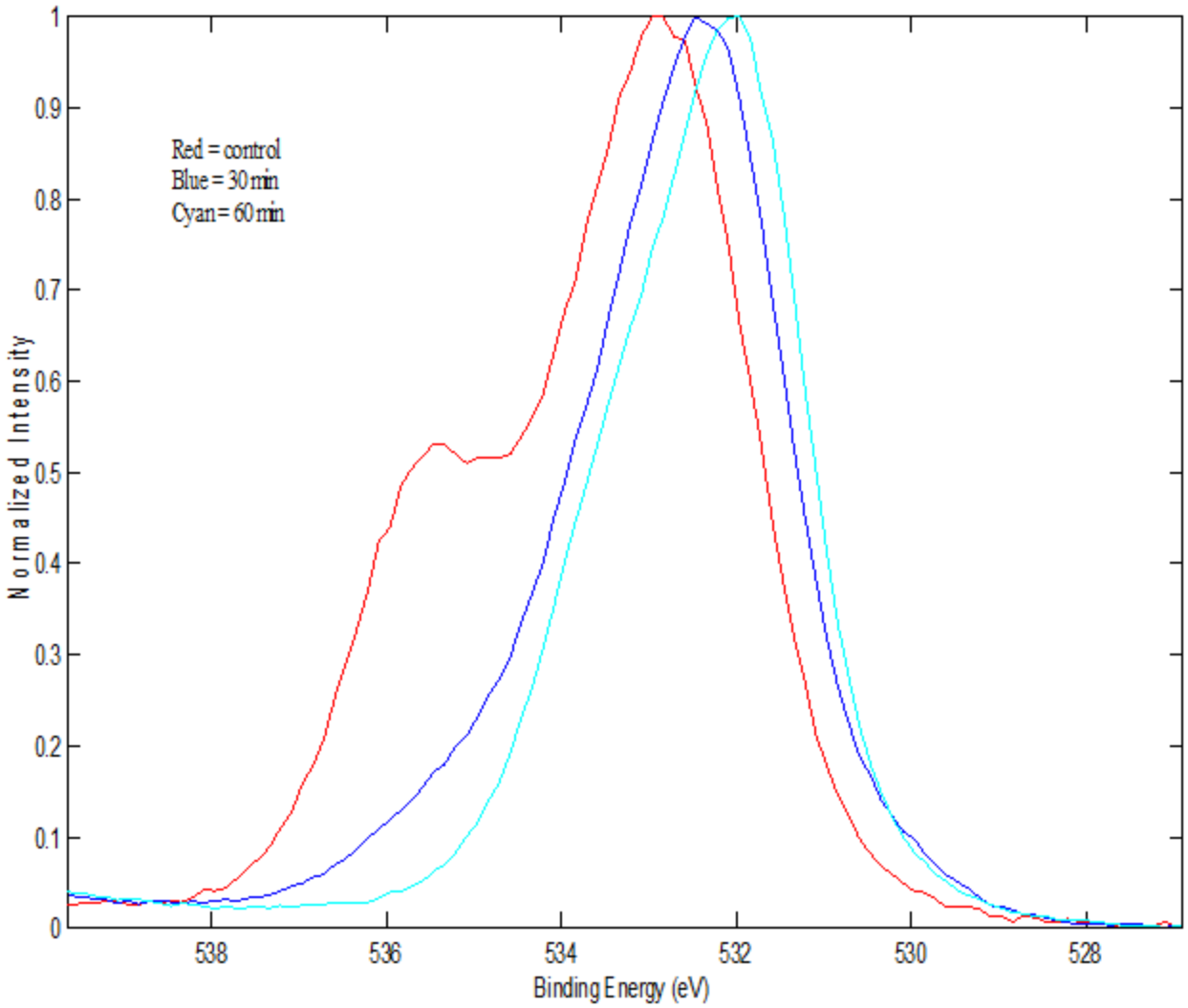

Figure 41: O 1s spectrum for the control and the grafted samples.

Assignment	Binding Energy (eV) [a]	0 min	30 min	60 min
O-C-C ‖ O*	531.5	0.0	13.6	17.6
HO-C=O*	532.2	46.8	52.6	55.9
*(H)O-C=O *O-C-C ‖ O	533.5	26.3	24.9	26.6
Nafion oxygen	535.2	26.8	8.9	0.0

Table 35: Results of the curve fitting for the O 1s spectra of the photo-oxidized Nafion films grafted to polyacrylic acid

5 DISCUSSIONS

5.1 Polystyrene

The polystyrene was surface treated by 3 different techniques. Polystyrene is known to absorb photons at both the radiations; 253.7 nm[33, 35] (Fig. 42) and 184.9 nm[34, 35] photons. The rate of functionalization is different for these 3 types of treatments (Fig.43).

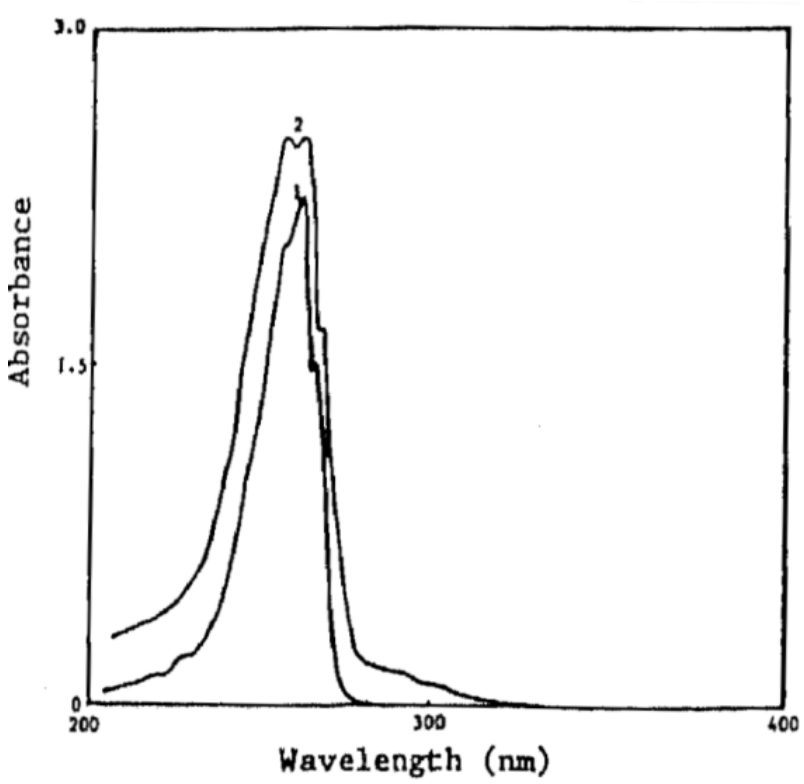

Figure 42: UV absorption spectrum of Ethyl benzene (1) and Polystyrene (2)[35]

XPS has demonstrated that treatment of polystyrene in the presence of oxygen and ultra-violet radiation of 184.9/253.7 nm results in significant oxidation of the surface (38.4 At %) which is in good agreement with previously reported value of 36- 38%. [28, 36, 37] A significant amount of oxygen is observed after only 1.5 minutes of treatment. After 20 minutes of treatment

the surface becomes saturated with oxygen. Photons from the 184.9 nm mercury lamps results in active species on the polymer backbone. The active species generated on the surface then react with the atomic oxygen and the oxygen molecules.

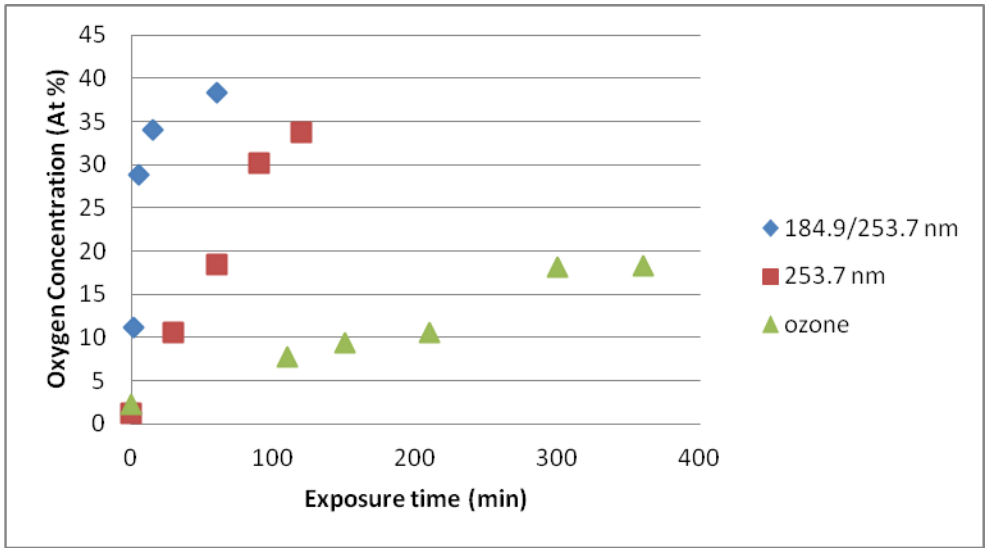

Figure 43: Atomic Oxygen Concentration over treatment time for Polystyrene surface activated by different techniques.

The second set of experiments used 253.7 nm mercury lamps. The surface oxidation in this technique is slower than the earlier technique. Since molecular oxygen remain unaffected in this radiation (Fig 9), the surface change is caused by the reaction of molecular oxygen with the active sites created on the polymer surface due to the 253.7 nm irradiation. Consistent with the results in this study, XPS analysis of UV photo-oxidized polystyrene with 240-600 nm photons, showed a loss of aromaticity by monitoring the Π→Π* shake-up satellite J.P.S Badyal et al have also reported similar moieties: C*-CO_2 (~285.5eV), C-O (~286.4eV), C=O (~287.7eV), and O-C=O (~289.3eV).[38]

Ozone treatment of polystyrene had the slowest rate of functionalization, understandably

since the radiation was not directly incident on the polymer surface. Ozone is well known to add across unsaturated carbon-carbon bonds, similar to the phenyl group in polystyrene, to form a primary ozonide that decomposes into an aldehyde or ketone and a Criegee intermediate.[39, 40] One disadvantage of the above treatments is the formation of a surface layer of low molecular weight oxidized material (LMWOM). A loosely bound surface layer so formed has been shown to have a detrimental effect on adhesion for number of polymer-adhesive systems.[41, 42]

Davidson et al.[28] performed methanol washing of polystyrene surface after UV-ozone treatment. Methanol wash reduced the atomic concentration of oxygen from 37.7 to 21.8% (Fig. 44).

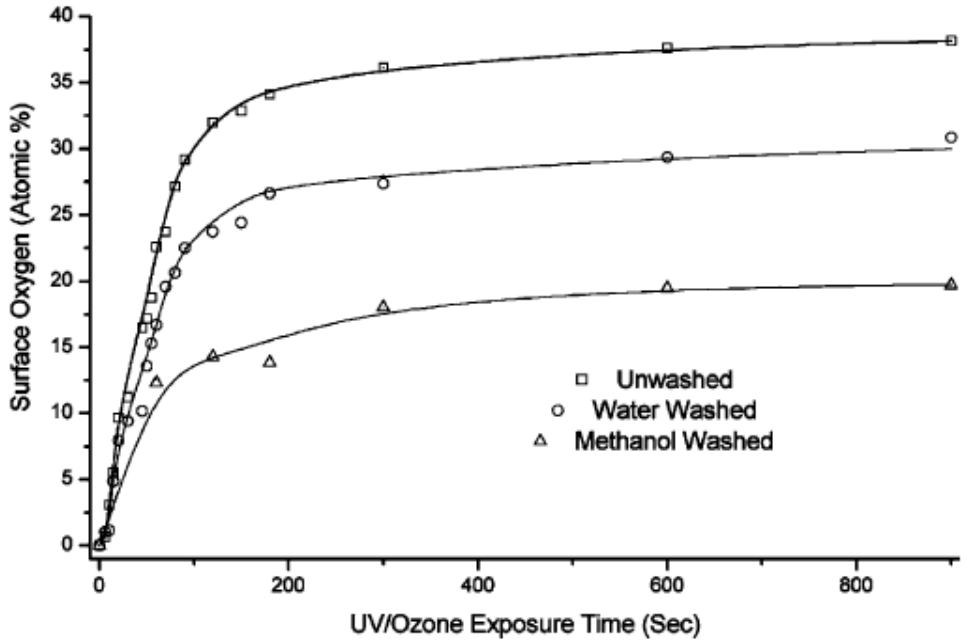

Figure 44: Oxygen concentration of the washed and unwashed as studied by Davidson et al.[28]

When polystyrene (PS) is radiated with radiation, free radicals (R•) are formed on the backbone of the PS, such as resulting from phenyl radical (Ph•) desorption as illustrated in reaction (6).[43] Subsequently, oxidation of R• (and PS•) may lead to alkoxyl radicals (RO•) by

reactions (9) and (10). The ether and alcohol groups may then be formed from the alkoxyl radicals via the cross-linking reaction (12) and abstraction of hydrogen from PS by reaction (13), respectively.

$$PS + 253.7\ nm \rightarrow R\bullet + Ph\bullet \quad (6)$$

$$R\bullet + O_2 \rightarrow RO_2\bullet \quad (7)$$

$$RO_2\bullet + PS \rightarrow ROOH + PS\bullet \quad (8)$$

$$RO_2\bullet + R\bullet \rightarrow 2RO\bullet \quad (9)$$

$$ROOH \rightarrow RO\bullet + OH\bullet \quad (10)$$

$$RO\bullet \rightarrow R'C{=}O + R''\bullet \quad (11)$$

$$RO\bullet + R\bullet \rightarrow ROR \quad (12)$$

$$RO\bullet + PS \rightarrow ROH + PS\bullet \quad (13)$$

Major contributors to the C 1s spectra for the grafted polystyrene samples were aromatic carbons. This suggests that the oxidized polystyrene was only partially coated with poly(acrylic acid). If only poly(acrylic acid) was present, the two O 1s peaks at 532.2 eV and 533.4 eV would have identical intensities[31] The surface does exhibit weak peaks due to acrylic acid indicating that the surface was thinly/partially coated. The grafting was partial possibly due to the presence of a layer of LMWOM over the polystyrene surface. A thick poly(acrylic acid) layer would have an O/C theoretical ratio of 0.67 compared to the lower values detected.

5.2 Nafion

The C 1s and O 1s spectra (Fig 38, 39) and quantitative analysis results for the Nafion control samples pretreated with 3% H_2O_2 (Table 23) are in good agreement with the literature.[22,32]

The photo-absorbed VUV photons emitted from the excited Ar atoms at 104.8 and 106.7 nm may initiate significant chemical effects to produce free radicals (R• and RO•). Since the VUV photon energies are greater than the C-O (~4 eV), C-C (~3 eV) and C-F (~5 eV) bond strengths,[44] the energetically possible reaction steps (14) - (16) are shown below with their photo-dissociation wavelengths for the polyfluorosulfonic acid (PSA) membrane.

$$PSA + h\nu = R_1\bullet + R_2\bullet \qquad \lambda \leq 410 \text{ nm} \qquad (14)$$

$$PSA + h\nu = R_3\bullet + R_4O\bullet \qquad \lambda \leq 310 \text{ nm} \qquad (15)$$

$$PSA + h\nu = R_5\bullet + F\bullet \qquad \lambda \leq 250 \text{ nm} \qquad (16)$$

Exposing Nafion (Fig. 3) to VUV photo-oxidation downstream from the Ar plasma results in defluorination of the surface, probably via C-C, C-O and C-F bond breakage as illustrated in reactions (14) - (16), respectively, and incorporation of oxygen at the surface from 8.3 to 12.3 at% after 60 min of treatment (Table 30).

Momose et al.[45] investigated surface modification of tetrafluoroethylene and perfluoroalkoxyvinyl ether copolymer (PFA) and polytetrafluoroethylene (PTFE) with Ar plasma treatment in a radio-frequency generator, where VUV radiation is one of the components of the plasma, and subsequent air exposure using XPS and electron spin resonance (ESR). Peroxy

radicals (ROO•) were observed with the development of a heavily cross-linked or branched structure incorporating oxygen at the surface. The peroxy radicals were attributed to two types of oxygen: one bonded to carbon in the cross-linked structure mostly at the surface and the other bonded to carbon arising from scission of the main chain mainly in the bulk of the polymer. Exposure of PFA at room temperature to γ-radiation produces nearly equal amounts of the main chain ($-CF_2-C^{\bullet}F-CF_2-$) and end-chain ($-CF_2-CF_2\bullet$) radicals with no evidence for scission of bonds at the perfluoropropyl vinyl ether sites.[46] Rasoul et al.[47] investigated UV photo-degradation of fluorinated ethylene propylene copolymer (FEP) using a high power xenon lamp at wavelengths greater than 200 nm and also observed by ESR chain scission free radicals which were transformed to peroxy radicals upon exposure to air. XPS analysis showed about a 2 at% of oxygen in the surface due to the formation of C=O groups along with the possible formation of cross-links between polymer chains probably resulting from reactions (17) - (19).

$$ROO\bullet + R^1\bullet = RO\bullet + R^1O\bullet \qquad (17)$$

$$RO\bullet = -CF_2-CF_2\bullet + -CF_2C(O)F \qquad (18)$$

$$R\bullet + R^1\bullet = R-R^1 \qquad (19)$$

$$RO\bullet + R^1\bullet = R-O-R^1 \qquad (20)$$

Fluorinated alkoxyl radicals have been previously reported to undergo chain scission through a weakened C-C bond to form carbonyl fluoride groups as shown in reaction (18).[48,49,50,51] The fluorinated alkoxyl radicals may also react to produce the observed oxygen incorp-oration into the polymer chain by reaction (20).

Additional incorporation of oxygen into the surface may occur by the reaction of atomic oxygen and/or ozone (produced from the reaction of atomic and molecular oxygen) with free radicals via reaction steps (21) and (22).

$$R\bullet + O(O_3) = RO\bullet + (O_2) \qquad (21)$$

$$ROO\bullet + O(O_3) = RO\bullet + (2)O_2 \qquad (22)$$

The XPS quantitative analysis results for pre-treated Nafion samples that were exposed to 0, 0.5 and 1 h of VUV photo-oxidation and then grafted with acrylic acid, H_2C=CH-COOH showed a decrease in F and an increase in C and O (Table 33 and Table 34) with VUV treatment time as expected when poly(acrylic acid) is effectively grafted to the modified Nafion substrate.

6 CONCLUSIONS

6.1 Polystyrene

The surface modification of polystyrene was performed by three techniques. Treatment of the polystyrene film for as little as 2 minutes with 253.7/184.9 nm radiation results in significant oxidation of the surface. With 253.7 nm photo-oxidation, a methodical increase in the atomic % of oxygen was observed up to 2 h of treatment time. Chemical state analysis showed the initial formation of C-O and C=O groups and then O-C=O type moieties. The contact angle measurements confirmed that the surface became more hydrophilic with increase in the treatment times. Ozone treatment was performed in the absence of radiation. This treatment was the least aggressive of the three techniques. Poly(acrylic acid) was grafted onto the activated surface. Poly(acrylic acid) was only thinly and/or partially grafted onto the modified surface after removal of a weak boundary layer formed during photo-oxidation.

6.2 Nafion

Vacuum UV (VUV) photo-oxidation of a polysulfonic acid membrane (Nafion-117) was studied downstream from low-pressure Ar microwave plasma. X-ray photoelectron spectroscopy (XPS) analysis showed de-fluorination and the incorporation of oxygen into the modified surface with increase in the treatment times. Poly(acrylic acid) was effectively grafted to the treated membrane surface.

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